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Recent Advances on Benzylidene Cyclopentanones as Visible light Photoinitiators of Polymerization

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Abstract

Photopolymerization is a rapidly evolving research field, supported by the growing demand for greener polymerization processes and the development of 3D printers used now for daily applications. With aim at developing dyes adapted for LEDs used in 3D printers, benzylidene cyclopentanones have been regarded as interesting structures due to their facile synthesis, low cost, high thermal and photochemical stability. Especially, benzylidene cyclopentanones proved to be better candidates than their benzylidene ketones analogue due to the rigidity provided by the central five-membered ring. As a result of this rigidification, higher monomer conversions could be obtained. Noticeably, benzylidene cyclopentanones could initiate one and two-photon polymerizations processes, what is relatively unusual for dyes to exhibit this dual photoinitiating ability. In this review, recent advances concerning benzylidene cyclopentanones are detailed. Compared to their acyclic analogues, a severe improvement of the photoinitiating ability has been demonstrated for benzylidene cyclopentanones, so that comparisons between these two families of photoinitiators is provided.

Keywords

Photoinitiator; benzylidene cyclopentanone; photopolymerization; LED; low light intensity

1. Introduction

During the past decades, a great deal of efforts has been devoted to develop greener and more sustainable polymerization processes.[1–4] With aim at reducing the environmental impact of polymerization processes through eco-responsible approaches, photopolymerization activated under low light intensity with light-emitting diodes (LEDs) or even with sunlight constitutes a promising alternative to the traditional thermal polymerization.[5–12] Compared to the traditional thermal polymerization which is carried out in solution and upon heating of the reaction medium, photopolymerization exhibits several advantages. Notably, photopolymerization can be carried out without solvents, avoiding the release of volatile organic compounds (VOC).[13] Photopolymerization processes can also be extremely fast, enabling to end the polymerization within a few seconds. A temporal and spatial control can also be obtained, meaning that only the surface which is exposed to light will polymerize and during the time the light is switched on. If historically, photopolymerization was done upon irradiation in the UV range, nowadays, this approach is more and more discarded in favor of visible light photopolymerization. Indeed, UV light is facing numerous safety concerns and is notably responsible of skin cancers and eye damages.[13–16] Ozone is also produced during polymerization, what constitutes another drawback of the UV approach.[13–16] To end, the light penetration which can be achieved in the UV range remains limited, not exceeding 600 μm at 350 nm, whereas this latter can reach 5 cm at 800 nm (See Figure 1).[17] Therefore, photopolymerization is nowadays facing a revolution, with the possibility to polymerize thick and even filled samples.[18]

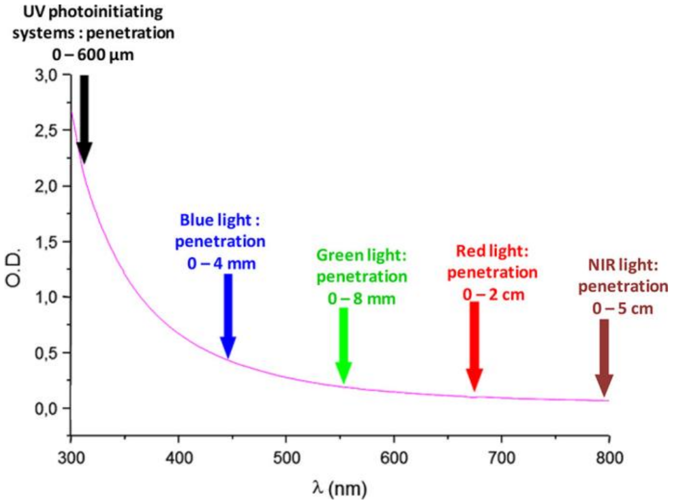


Figure 1. Light penetration in a polystyrene latex with an average diameter of 112 nm. Reprinted with permission from Bonardi et al.[17]

Interest for photopolymerization is also supported by the different applications where photopolymerization is nowadays unavoidable.[2,18–35] Notably, photopolymerization is widely used in applications such as 3D and 4D printing, microelectronics, adhesives, coatings and dentistry.[36–45] Besides, if use of visible light for photopolymerization constitutes an appealing approach, the fact to use less energetic photons adversely affect the monomer conversion that can be achieved by visible light photoinitiators compared to their UV analogues. This is the reason why since approximately 15 years, a great deal of efforts has been devoted to examine a maximum of families of dyes in order to address the reactivity issue. Among these families of dyes, dithienophospholes,[46,47] zinc complexes,[48] diketopyrrolopyrroles,[49–51] iridium complexes,[52–59] metal organic framework (MOFs),[60–62] helicenes,[63,64] benzylidene ketones,[65,66] phenothiazines,[67–77] camphorquinones,[78,79] curcumin,[80–83] push-pull dyes,[6,7,84–96] coumarins,[97–109] perylenes,[110–113] 2,3-diphenylquinoxaline derivatives,[114,115] viologen derivatives,[116–118] copper complexes,[119–136] thiophene derivatives,[137] acridine-1,8-diones,[138–140] chromones and flavones,[141–143] polyoxometalates,[144–146] perovskites,[147,148] pyrenes,[149–157] truxene derivatives[158] conjugated polymers,[159] iodonium salts,[160–167] chalcones,[44,168–180] cyanines,[181–187] Schiff bases,[188] thioxanthones,[189–202] iron complexes,[61,84,203–208] Bodipy,[209–214] cyclohexanones,[215–218] benzylidene ketones,[65,66,219–222] carbazoles,[223–236] benzophenones,[237–244] pyrrole derivatives,[245] anthracene,[246] acridones,[247,248] *N*-heterocyclic carbene boranes,[249] phenazines,[250] naphthoquinones,[251] silyl glyoximides,[252] imidazole derivatives,[253] pyridinium salts,[254] dihydroanthraquinones,[255] porphyrins,[256,257] triphenylamines,[258,259] naphthalimides [160,260–277] and squaraines [278–282] can be cited as the main families examined for their photochemical reactivities.

Among dyes that were developed for photopolymerization, only few structures can be indifferently used to initiate one photon or two photon polymerization processes. In this field, benzylidene cyclopentanones can be cited as a relevant example of this. These structures are not only used in photopolymerization but also for photodynamic therapy,[220,221,283–285] and for their photophysical properties.[286,287] Interest of these structures relies in their easy synthetic access since these dyes can be prepared in one step by mean of a crossed aldol condensation reaction between an aldehyde and cyclopentanone in basic conditions, in solution or in solvent-free conditions.[288,289] First reports mentioning the use of benzylidene cyclopentanones as photoinitiators for UV photopolymerization were published as soon as 1991, concomitantly by Monroe and coworkers as dyes for the sensitization of *o*-chlorohexaarylbisimidazoles (HABI) [290] and by Yang and coworkers for the sensitization of diphenyliodonium hexafluorophosphate.[291] In this last work, a high intensity xenon lamp (I = 400 W) was used to initiate the free radical polymerization (FRP) of methyl methacrylate (MMA). In this early work, the strong inhibition effect of oxygen on the FRP of MMA was clearly demonstrated.[292] Since then, numerous structures have been developed. Especially, symmetrically and asymmetrically benzylidene ketones have been proposed in order to optimize their two-photon absorption properties or their solubilities in monomers. In this review, an overview of the recent advances on visible light benzylidene cyclopentanones is provided. To evidence the interest of these symmetrical or asymmetrical structures, comparisons with benchmark photoinitiators is provided.

2. Symmetrically substituted benzylidene cyclopentanones

Two-photon polymerization is a polymerization technique making use of dyes capable to initiate two photon absorption (TPA) processes, meaning that the molecule can absorb simultaneously two photons in the same quantum event.[293–297] Since the pioneering works of Maruo in 1997 who succeeded to design a 3D structure by two-photon polymerization, this polymerization technique has become the focus of intense research efforts and numerous major achievements have been obtained.[298–303] Besides, there are still remarkable challenges and issues to address.[77,304–308] As specificities, due to the quadratic dependency of TPA, the two-photon absorption process is limited to a small volume in close vicinity to the laser point. As a result of this, two-photon polymerization is limited to the microfabrication of three-dimensional objects of micrometer sizes but enables to produce these objects with an exceptional spatial resolution that cannot be obtained by one-photon polymerization.[309] In 2012, a series of photoacid generators of high-sensitivity for two-photon polymerization were proposed by Wu and coworkers.[310] It consisted in the sensitization of a photoacid generator by mean of a two-photon chromophore (See Figure 2). This approach is less complicated than the covalent linkage of the two partners, as exemplified by several examples reported in the literature.[311–313] In the case of 2,5-*bis*(4-(diphenylamino)benzylidene)cyclopentan-1-one (BDPA) and 1,5-*bis*(4-(diphenylamino)phenyl)penta-1,4-dien-3-one (BDPO), triphenylamines were introduced as peripheral groups as the pKa of the protonated form of triphenylamino groups is equal to - 5. As photoacid generator, the none-ionic *N*-(trifluoromethanesulfonyloxy)-1,8-naphthalimide (NIOTf) was selected to build the two-photon acid generation systems. To evidence the interest of introducing cyclopentanone as the central group in BDPA, a comparison was established with DBPO prepared with acetone. Finally, 4-diethylamino groups were introduced as peripheral groups of 2,5-*bis*(4-(diethylamino)benzylidene)cyclopentan-1-one (BDEA) in order this time to investigate the benefits of the peripheral groups in BDPO.

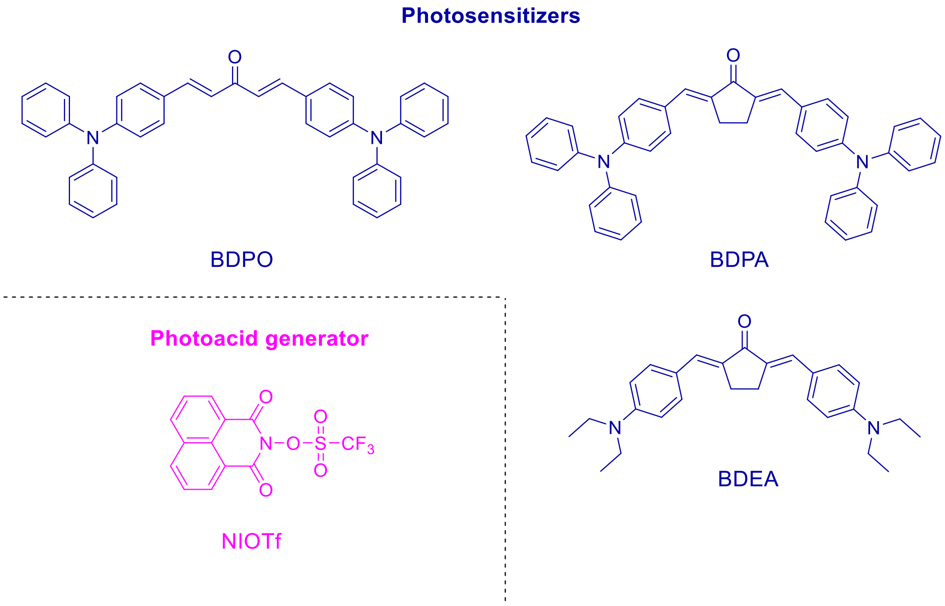


Figure 2. Chemical structures of BDPO, BDPA, BDEA and NIOTf.

Noticeably, examination of their absorption properties revealed the cylopentanone linkage to induce a redshift of the absorption of BDPA (λ_{max} = 459 nm) compared to the flexible linkage used in BDPO (λ_{max} = 433 nm) by enabling to get a higher electronic delocalization. A strong absorption band was found in the visible range for the two dyes, in the 350-500 nm range assigned to an intramolecular charge transfer (ICT) band between the electron-donating peripheral groups (triphenylamines, diethylaminophenyl groups) and the central electron-withdrawing ketone (See Figure 3).

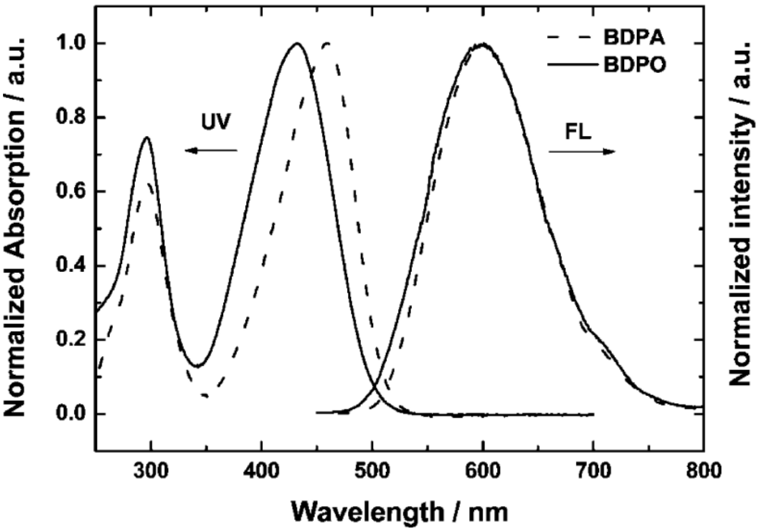


Figure 3. UV-visible absorption spectra of BDPA and BDPO in acetonitrile. Reproduced with permission of Ref. [310]

Despite different absorption maxima, similar emission maxima were determined for BDPA and BDPO, located at 600 nm. Photoluminescence quantum yields of 0.05 and 0.027 were respectively determined for BDPA and BDPO, once again demonstrating that the higher flexibility in BDPO was favoring nonradiative deactivation pathways, contributing to decrease the photoluminescence quantum yield. Examination of their two-photon absorption properties in acetonitrile revealed BDPA and BDPO to exhibit maxima located at 820 and 760 nm, therefore blue-shifted compared to the double wavelengths of their absorption peaks. It was thus concluded that BDPA and BDPO could reach excited states of different parity compared to that achieved by one-photon absorption.[314] A higher two-photon absorption cross-section was found for BDPA compared to BDEA also comprising a cylcopentanone spacer, assigned to an extended π-conjugation due to the presence of triphenylamino groups (See Figure 4).[315] Comparison between BDPA and BDPO both comprising peripheral triphenylamino groups revealed the two-photon cross-section of BDPO to be lower than that of BDPA, once again originating from a higher structural flexibility in BDPO.

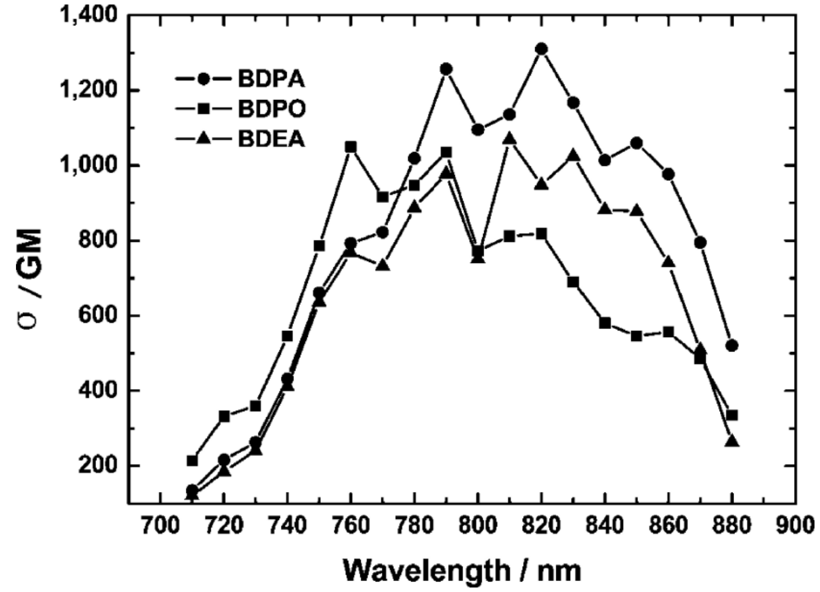
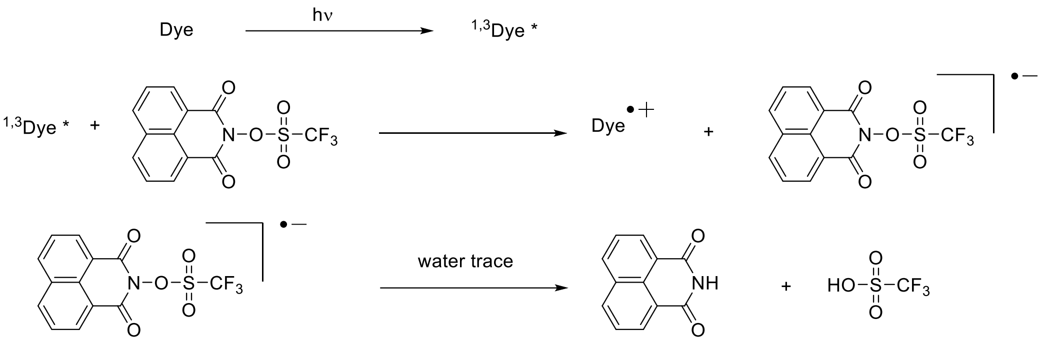


Figure 4. Two-photon excitation spectra for BDPA, BDPO, and BDEA in acetonitrile. Reproduced with permission of Ref. [310]

From the Rehm−Weller equation, a favorable thermodynamic interaction between the excited dyes and NIOTf could be determined, free energy changes of - 12.2 and - 13.4 kcal/mol between respectively determined for the two-component BDPA/NIOTf and BDPO/NIOTf systems.[316,317] This favorable interaction was confirmed by fluorescence quenching experiments, fluorescence quenching constants (k_q) of 1.30 and 1.38 × 10^{10} $L.M^{-1}.s^{-1}$ being respectively determined for BDPA and BDPO, and demonstrating that the interaction was diffusion controlled in acetonitrile.[318] Photoacid generation with the different two-component dye/NIOTf systems upon excitation at 473 nm was demonstrated by adding Rhodamine B base to the acetonitrile solutions, resulting in the appearance of a characteristic absorption band at 555 nm. Meanwhile, a photobleaching of the dyes was jointly observed, resulting from the photoinduced electron transfer from the dyes towards NIOTf. Overall, the following mechanism of photoacid generation was proposed. Thus, upon excitation of the dyes, a photoinduced electron transfer can occur between the excited dyes and NIOTf. The resulting radical anion can then react with water traces, producing trifluoromethanesulfonic acid (See Scheme 1).[319,320] First investigations revealed the singlet and the triplet excited states of dyes to be both involved in the reaction with NIOTf. To evidence this, addition of anthracene in acetonitrile solution drastically impacted photoacid generation, anthracene being a well-known triplet quencher.[318,320]



Scheme 1. Mechanism of photoacid generation.

Photoacid generation of these different systems were evaluated by investigating the acid-catalyzed deprotection of a partially *tert*-BOC-protected poly(*p*-hydroxystyrene) (PBOCS). Efficiency of the deprotection was compared with that performed with the two-component ITX/NIOTf where ITX stands for 2-isopropylthioxanthone. Upon irradiation with a near-IR femtosecond laser, the two-component ITX/NIOTf showed deprotection ability comparable to that obtained with NIOTf alone. Noticeably, if the two-component BDEA/ NIOTf system was almost inefficient to induce the deprotection of PBOCS, conversely, a remarkable deprotection ability was demonstrated with the BDPO and BDPA-based system, the highest deprotection rates being obtained for the rigid BDPA which exhibit the highest fluorescence quantum yield and the largest two photon absorption cross-section of the series.

Finally, interest of these structures was demonstrated by performing two-photon lithography. By photoacid generation, the deprotective reaction converted the *tert*-BOC-protected poly(*p*-hydroxystyrene) polymer as hydroxyl-containing polymer, rendering the exposed material soluble in basic aqueous solution and thus to basic developer. As shown in the Figure 5, well-defined structures could be obtained upon irradiation with a laser power of 0.5 mW and a scan speed of 110 μm/s. Compared to the reference ITX/NIOTf system, the newly developed photoacid generator systems required a laser power (0.24 mW) twice lower than that required with the reference system utilizing ITX as the sensitizer.[311]

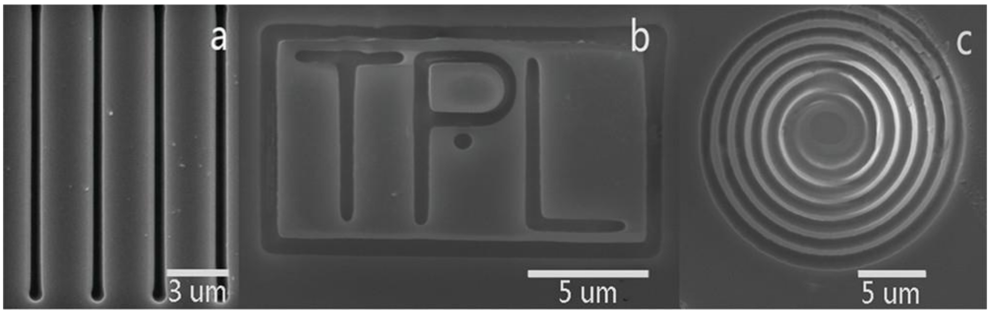


Figure 5. 3D patterns obtained with the two-component BDPO/NIOTf system at a laser power of 0.24 mW and a scan speed of 10 μm/s. Reproduced with permission of Ref. [310]

The same year, another group investigated the incorporation of benzylidene cyclopentanones into epoxy polymers so that the benzylidene cyclopentanones could act first as a co-monomer with epichlorohydrin (See Figure 6) and in a second time, it could act as a photosensitizer to initiate photocrosslinking of polymer chains by mean of 2π+2π cycloaddition reactions (See Scheme 2).[321] In this aim, 2,5-*bis*(4-hydroxy-3-methoxy-benzylidene)cyclopentanone (BHMBCP) was selected as the photosensitive monomer capable to react by polycondensation with epichlorohydrin in basic conditions. Epoxy-based polymers are extensively studied as the volume shrinkage is considerably reduced compared to that observed with poly(acrylates).[322–326]

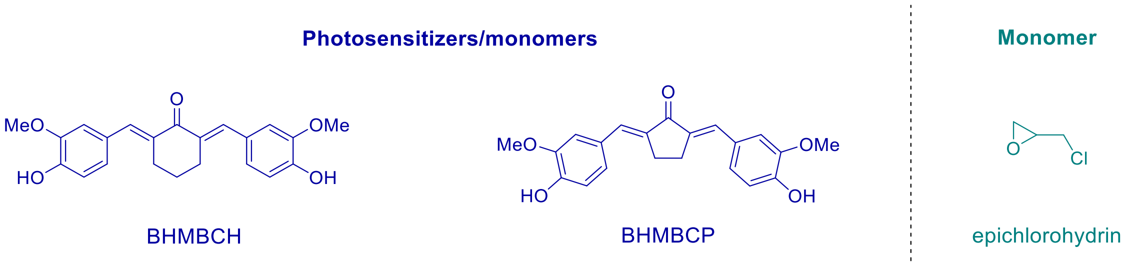
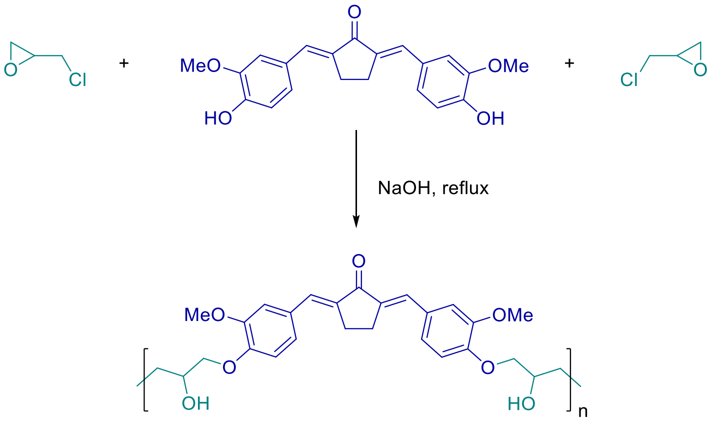


Figure 6. Chemical structures of BHMBCP, BHMBCH and epichlorohydrin.



Scheme 2. Synthetic route to BHMBCP-based polymers.

Epoxy-based polymers comprising BHMBCP as the photosensitive unit proved to be soluble in most of the common organic solvents such as THF, DMF, DMSO, dioxane and halogenated solvents. Comparison with epoxy-based polymers comprising BHMBCH revealed these polymers to be more soluble than those prepared with BHMBCP, attributable to the tridimensionality of cyclohexanone adversely impeding the packing of the polymer chains.[327] Noticeably, analyses of the thermal properties of epoxy polymers revealed the thermal stability to be improved for BHMBCP-based polymer compared to its BHMBCH analogue. Thus, depending on the percentage of benzylidene cyclopentanone introduced, decomposition temperatures ranging between 459 and 487°C were determined by thermogravimetric analysis (TGA) for BHMBCH-based polymers, lower than that determined for BHMBCP-based polymers (520-854°C). Increase of the decomposition temperature for BHMBCP-based polymers was assigned to a higher heat combustion of cyclopentanone compared to cyclohexanone,[328]but also to the higher planarity of cyclopentanone favoring interchain interactions. Interestingly, the highest decomposition temperatures were determined for all polymers comprising the highest ratio of epichlorohydrin (1:200 benzylidene cyclopentanone:epichlorohydrin). By Differential Scanning Calorimetry (DSC) measurements, crosslinking temperatures in the 325-335°C range for BHMBCH-based polymers and in the 399-408°C range for the BHMBCP-based polymers were determined, consistent with the values determined by TGA measurements. Photocrosslinking of the polymer chains could also be obtained upon irradiation with a medium pressure mercury vapor lamp. By UV-visible absorption spectroscopy, decrease of the absorption peak at 379 nm corresponding to π-π* transitions of the olefinic double bonds was observed, resulting from the photoinduced 2π+2π cycloaddition reaction. As anticipated, a higher photocrosslinking ability was found for all cyclopentanone-based polymers compared to their cyclohexanone-based analogues, consistent with stronger interactions of the polymer chains in the case of cyclopentanone favoring crosslinking.

In 2013, Liska and coworkers demonstrated the crucial role of the size of the central ring on the photoinitiating ability of a series of benzylidene ketones.[305] Indeed, size of the ring can affect photophysical properties such as fluorescence. Thus, benzylidene cyclohexanones are well-known to be less emissive than those based on cyclopentanones.[329] This point is of crucial importance considering that, in order to design two-photon photoinitiators and with aim at favoring the triplet deexcitation pathway, dyes exhibiting a low photoluminescence quantum yield are preferred.[330] To examine this point, a series of five compounds BZC1-BZC5 was designed and synthesized. Photoinitiating ability of dyes were compared to that of a reference compound, namely 4,4'-(2,5-dimethoxy-1,4-phenylene)*bis*(ethene-2,1-diyl))*bis*(*N,N*-dibutylaniline) R1 (See Figure 7).[331] From a synthetic viewpoint, the different dyes BZC1-BZC5 are cheap, considering that the crossed aldol condensation reaction could be carried out using cheap reagents (cyclopentanone, cyclohexanone, 4-dimethylaminobenzaldehyde) and sodium hydroxide as the base. Investigation of the absorption properties in dichloromethane revealed their absorption maxima to range from 430 nm for BZC4 and BZC5 up to 480 nm for BZC3 (See Figure 8). Thus, based on their absorptions, a redshift of the absorption maxima was found for dyes comprising as the central core, cyclohexyl (BZC4, BZC5) > acyclic (BZC1) > cyclopentyl (BZC2, BZC3) moieties. This trend is consistent with previous works reported in the literature.[332] An additional bathochromic shift could be obtained by replacing the dimethylamino group of BZC2 by a dibutylamino group in BZC3 (466 nm for BZC2 and 481 nm for BZC3). Noticeably, no difference on the absorption spectra of BZC4 and BZC5 was found, the methyl group in BZC5 being in a none-conjugated position with the rest of the molecule. By theoretical calculations, composition of the absorption band detected at low energy was determined as being an admixture of n-π* and π-π* transitions.

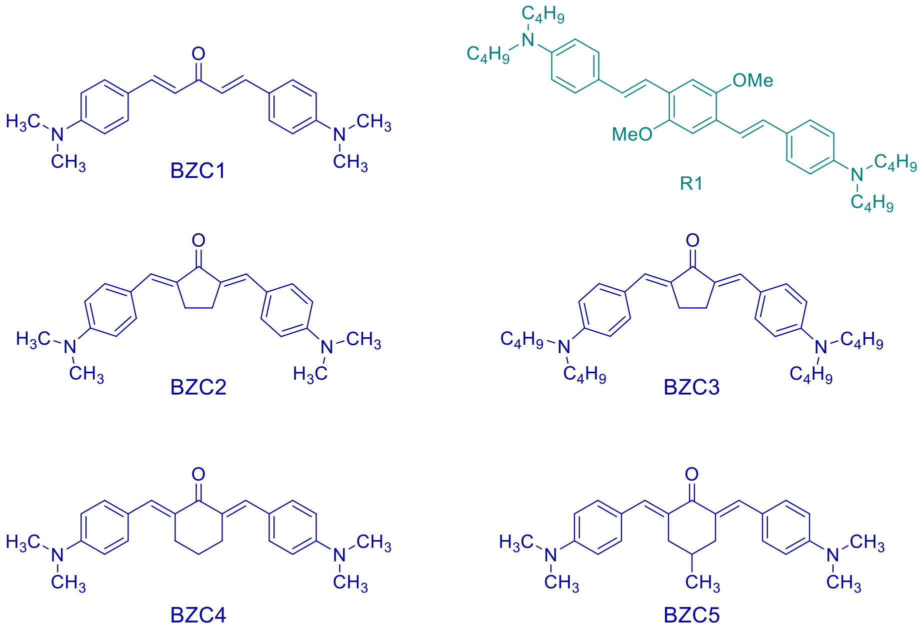


Figure 7. Chemical structures of BZC1-BZC5 and reference compound R1.

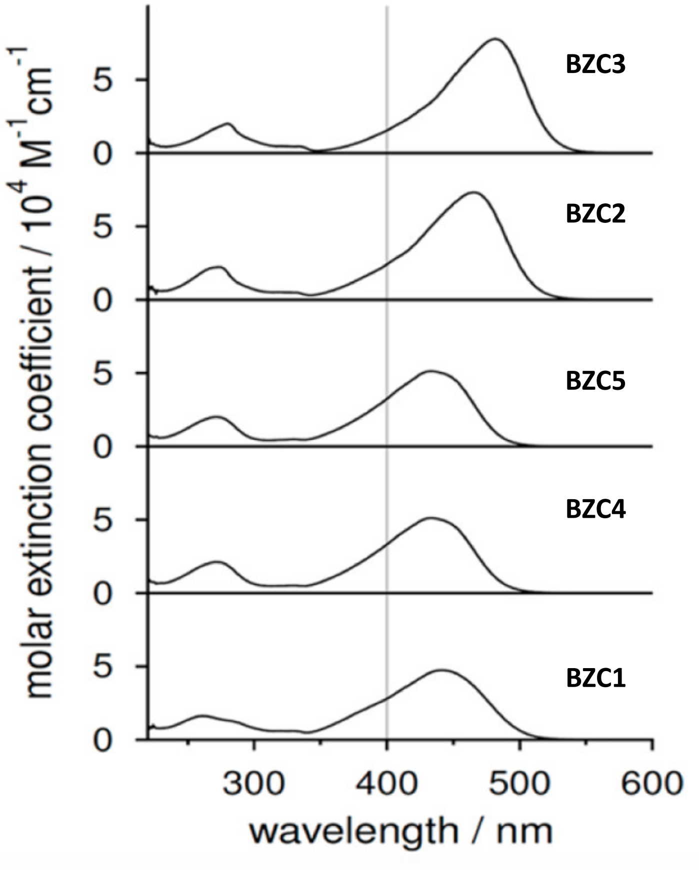


Figure 8. UV-visible absorption spectra of BZC1-BZC5 in dichloromethane. Reproduced with permission of Ref. [305]

Fluorescence properties of all dyes proved these structures to be highly sensitive to the solvent polarity, contrarily to what was observed for the reference compound R1.[306] Thus, upon increase of the solvent polarity, an enhancement of the photoluminescence quantum yield was observed, resulting from a decrease of the S_0-S_1 energy gap. In fact, the S_1 state of benzylidene ketones is a $\pi\pi^*$ state close to the triplet state ($n\pi^*$ state) so that an intersystem crossing can facilely occur according to the El-Sayed rules, constituting an efficient nonradiative deactivation channel.[333–335] By increasing the solvent polarity, a bathochromic shift of the singlet state occurs whereas an hypsochromic shift occurs for the $n\pi^*$ triplet state. As a result, an increase of the energy gap between the two states can be obtained, reducing the contribution of the intersystem crossing to the nonradiative deactivation pathways and contributing to increase the photoluminescence quantum yield. Considering that the polymerization efficiency of benzylidene ketones is strongly related to the efficiency of radical generation, their reactivities towards monomers but also to the two-photon absorption cross section, this latter was thus determined for all dyes, using chloroform as the solvent and upon excitation at 800 nm. If a two-photon absorption cross section of 349 GM was determined for BZC1, this value increased up to 466 GM of BZC2 comprising a cyclopentanone spacer. An opposite trend was found for BZC2 in which the peripheral dimethylamino group have been replaced by dibutylamino group and the two-photon cross section decreased to 327 GM. This unexpected result was assigned to the deformation of the central cyclopentanone ring induced by the bulky dibutylamino groups. By increasing the size of the central ring, a severe reduction of the two-photon cross section was found for BZC4 and BZC5, assigned to the nonplanarity of the six-membered ring. An additional reduction of the two-photon absorption cross section was found for BZC5 (191 GM vs. 352 GM for BZC4), demonstrating that the substitution of the central ring could significantly affect the two-photon absorption behavior.

Recently, in 2019, a crosslinkable version of BZC2 i.e. (2-oxocyclopentane-1,3-diylidene)*bis*(methanylylidene))*bis*(4,1-phenylene))*bis*(methylazanediyl))*bis*(methylene) diacrylate (PBDA) containing acryloyl groups was reported in the literature for one-photon and two-photon polymerization processes and developed for the design of biosafety materials (See Figure 9).[336] Indeed, migratability of photoinitiators within the polymer network can constitute a drastic limitation for the end-use of polymers, notably for applications such as food packaging or dentistry. This is the reason why a great deal of efforts is currently devoted to develop crosslinkable photoinitiators.[158,194,196,197,337–349] Parallel to this, benzylidene ketones have a wide spectrum of biological activities.[350–353] In the present case, due to the presence of acryloyl groups, PBDA could be efficiently crosslinked to the polymer networks, decreasing its migration ability. When one-photon polymerization experiments were carried out upon irradiation at 473 nm with a laser diode, polymerization of ethoxylated trimethylolpropane triacrylate (ETPTA) or poly(ethylene glycol)diacrylate (PEGDA) could be induced, even if the polymerization processes remained slow. Indeed, polymerization times of 16 min. were necessary to get acceptable monomer conversions. Thus, monomer conversions around 40% could be determined for the two monomers while using BDEA as the photoinitiator. Conversely, higher monomer conversions could be obtained with PBDA since conversions ranging between 50 and 80% could be determined after 16 min. of irradiation. For comparison, monomer conversions obtained with eosin were drastically low in the same conditions, remaining lower than 10%. Noticeably, higher monomer conversions were obtained with PEGDA than with ETPTA, indicating that the polymerization rates and final monomer conversions were strongly related to the type of monomer used. Indeed, ETPTA being a trifunctional monomer, formation of a highly crosslinked polymer network occurs more rapidly than with the difunctional monomer PEDGA, rapidly inhibiting the diffusion rate of free radicals and lowering the final monomer conversion.

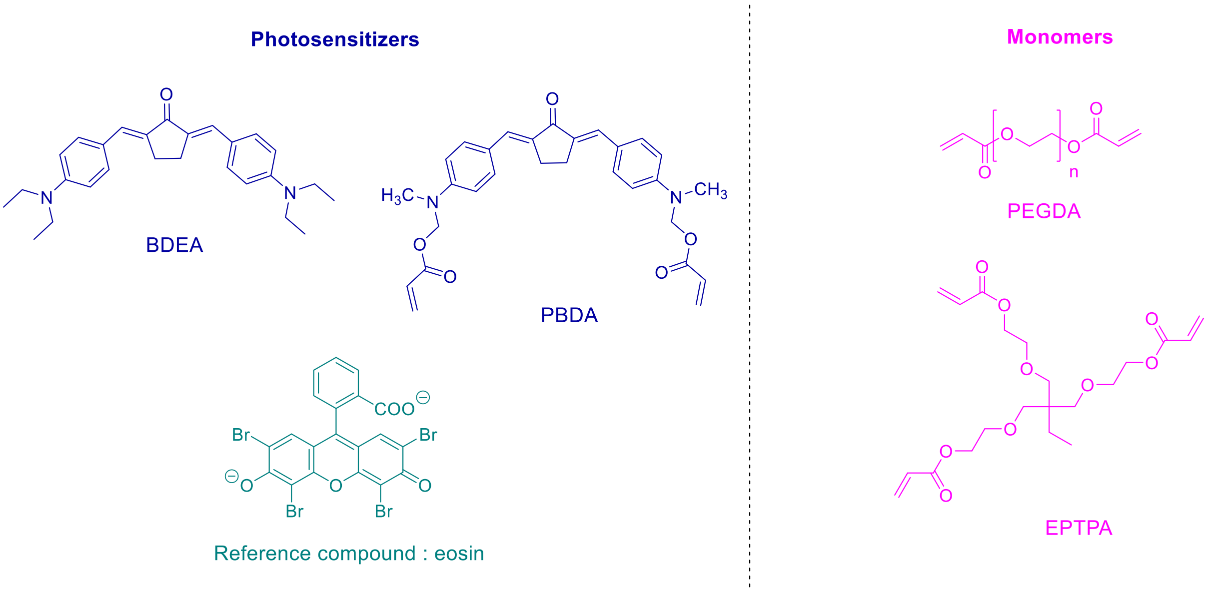


Figure 9. Chemical structures of BDEA and its crosslinkable version PBDA, EPTPA and PEGDA as monomers, and eosin used as a reference compound.

PBDA could also initiate the two-photon photopolymerization of the high-viscosity monomer EPTPA and decreased its migration ability within the polymer network. Noticeably, introduction of the two acrylate groups did not drastically modify the solubility of PBDA in EPTPA. Thus, use of 20 wt% DMSO as the solvent and 0.1 wt% of dye enabled to produce resins in which the dyes was perfectly dissolved. Biocompatibility of the PEGDA-based polymeric samples was examined by investigating the L929 cell viability after 48 h cultivation on polymeric substrates. Compared to the control group cultivated in polystyrene, a cell viability of 85% for the samples polymerized with BDEA and 100% for those prepared with PBDA could be determined.

In 2022, a new version of crosslinkable photoinitiator i.e. (2-oxocyclopentane-1,3-diylidene)*bis*(methanylylidene))*bis*(4,1-phenylene))*bis*(azanetriyl))tetrakis(ethane-2,1-diyl) tetraacrylate (4Met-BAC) enabling to improve its crosslinking ability compared to PBDA due to a higher number of crosslinkable functions was proposed by Chesnokov and coworkers (See Figure 10).[354] Parallel to this and based on previous works done by Liefeith and coworkers [355] mentioning the high solubility of the tetraester benzylidene ketone ((((2-oxocyclopentane-1,3-diylidene)*bis*(methanylylidene))*bis*(4,1-phenylene))*bis*(azanetriyl)) *tetrakis*(ethane-2,1-diyl) tetraacetate BA740 (in high viscosity monomers such as urethanedimethacrylate (UDMA) or biodegradable lactide-caprolactonemethacrylate (LCM) macromonomers. An improved solubility of 4Met-BAC in high viscosity monomers can thus be anticipated compared to that of PBDA. Therefore, by developing 4Met-BAC, a combination of two different and complementary approaches can be obtained, namely a good solubility of 4Met-BAC in the high-viscosity monomer pentaerythritol triacrylate (PETA) and a low migration ability in polymers. Noticeably, examination of the solvatochromism of 4Met-BAC in solvents of different polarities revealed this dye to exhibit a positive solvatochromism, with a variation of the position of the intramolecular charge transfer (ICT) band from 32 nm between toluene and DMSO. This redshift was assigned to a higher polarity of the excited state compared to the ground state. It also evidences the intramolecular change transfer existing between the electron-donating amino groups to the electrodeficient carbonyl group.[336] Noticeably, photoluminescence quantum yield of 4Met-BAC was low, around 0.09 and an excited state lifetime of 12.9 ns could be determined. A two-photon absorption cross section of 147 GM was measured by Z-scan experiments at 800 nm, consistent with the values determined for previous benzylidene ketones.[356]

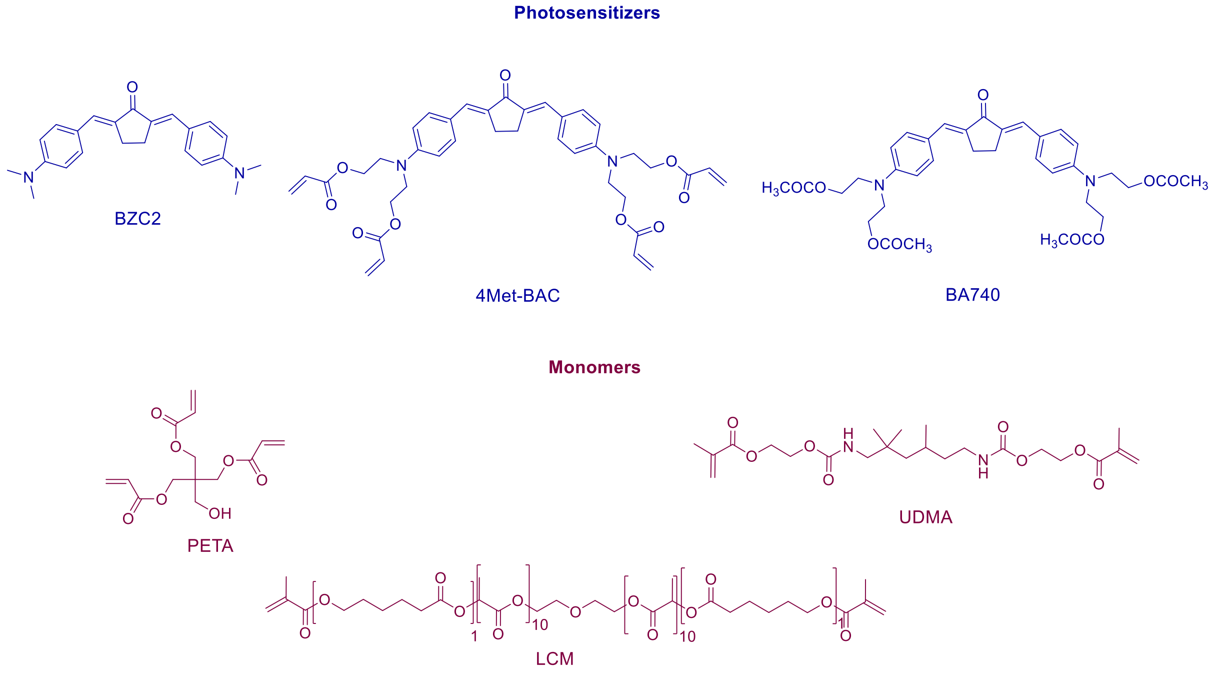


Figure 10. Chemical structures of 4Met-BAC, BZC2, BA740 and different monomers used for this study.

Photolysis experiments revealed 2,5-*bis*(4-(dimethylamino)benzylidene)cyclopentan-1-one (BZC2) and 4Met-BAC to exhibit slow photolysis rates (See Figure 11). Noticeably, photolysis of BZC2 was faster than that of 4Met-BAC. Photodegradation of the two dyes was determined as occurring in two steps. First, an intra- or an intermolecular electron transfer can occur with the formation of radical cation and radical anion pairs. Then, by proton transfer, ketyl radicals and aminyl radicals can form, constituting initiating radicals.

Photopolymerization experiments carried out at 380 nm (I = 210 mW/cm²) revealed BZC2 and 4Met-BAC to be capable to initiate a polymerization process, even when used as monocomponent systems. Thus, final monomer conversions of 10 and 21% could be determined during the polymerization of PETA after 300 s of irradiation for BZC2 and 4Met-BAC respectively. Higher monomer conversions obtained with 4Met-BAC compared to BZC2 was assigned to the higher solubility of 4Met-BAC in resins, improving the monomer conversion. Upon addition of dimethylaniline (DMA) or triethanolamine (TEA), an improvement of the monomer conversions could be evidenced, the conversions reaching at 35 and 33% respectively. However, these conversions remain low compared to that obtained for other photoinitiating systems previously reported in the literature.[45,357,358] Examination of the migration properties of photoinitiators in DMSO revealed the extractability of BZC2 to be 8 times higher than that of 4Met-BAC, consistent with its inability to crosslink to the polymer network. In the case of 4Met-BAC, an extractability of 13% from the polymer sample could be determined after a soaking time of 20 days in DMSO. By using a 4Met-BAC/AIBN combination, extractability of 4Met-BAC could even be totally suppressed, evidencing that the crosslinkable photoinitiator could be efficiently incorporated into the structure of the final polymer.

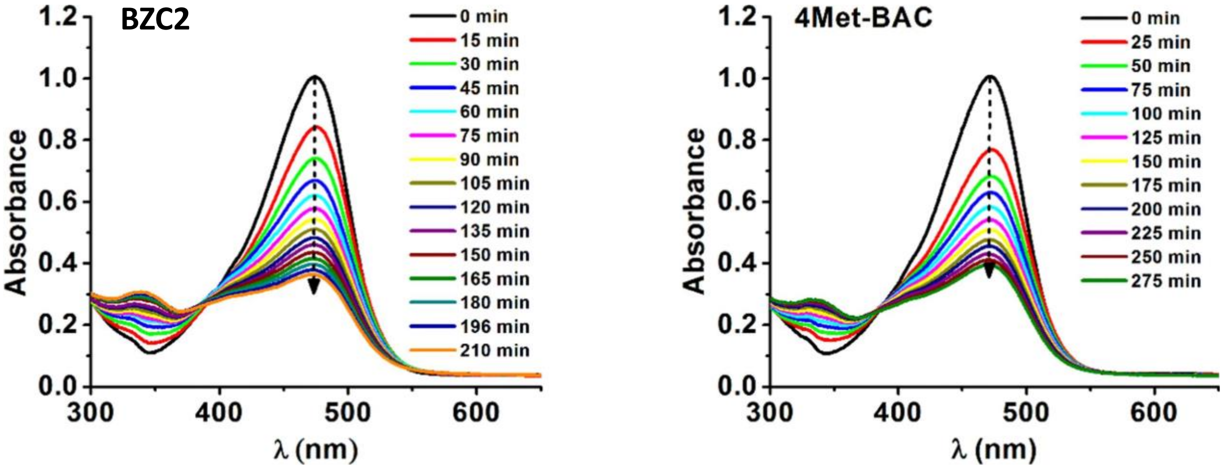


Figure 11. Photolysis of BZC2 and 4Met-BAC upon irradiation at 380 nm with a LED. Reproduced with permission of Ref. [354]

MTT cytotoxicity tests were carried out to examine the cytotoxicity of BZC2 and 4Met-BAC in polymers. In this aim, extraction times of the different samples were varied. Cytotoxicity tests revealed the BZC2/AIBN polymers to exhibit a pronounced cytotoxicity rank (CR) of 3 after one day of extraction whereas a CR of 1 was determined for the 4Met-BAC/AIBN samples. After seven days of extraction, no cytotoxicity was detected anymore for the 4Met-BAC/AIBN samples whereas the BZC2/AIBN polymers still remained toxic. Culture of fibroblasts on 4Met-BAC/AIBN-based samples revealed a good adhesion of the cells, with cells exhibiting typical fusiform or stellate shapes and a uniform distribution over the whole surface of the samples. Investigation of two-photon polymerization showed BZC2 to exhibit a smaller fabrication window than 4Met-BAC (17-30 mW vs. 6-50 mW for 4Met-BAC). Here again, a significant decrease of the dye washout from the polymers could be evidenced for 4MET-based polymers.

In 2015, Gryko and coworkers carried out a similar study, where a library of π-extended D-π-A-π-D benzylidene ketones was designed and synthesized with aim at examining the influence of the size of the central ketone ring on the photoinitiating ability.[359] Six four-, five- and six-membered ring compounds BZC6-BZC11 were prepared, enabling to design compounds exhibiting major differences in terms of rigidity (See Figure 12). Noticeably, despites their highly planar and π-conjugated structures, all dyes proved to be remarkably soluble in most of the common organic solvents. As evidenced by previous works, all dyes absorb light in the 400–550 nm range, once again evidencing the limited impacted of the central ring on the optical properties. Indeed, due to its aliphatic nature, the central core can only marginally impact the electronic delocalization occurring with the peripheral groups. Precisely, if absorption maxima of 2,4-*bis*(4-(dimethylamino)benzylidene)cyclobutan-1-one BZC6 and 2,4-*bis*(4-(didodecylamino)benzylidene)cyclobutan-1-one BZC7 were both located at 476 and 477 nm respectively in toluene, these values blue-shifted to 467, 466 and 440 nm for 2,4-*bis*(4-(4-(didodecylamino)styryl)benzylidene)cyclobutan-1-one (BZC8), 2,5-*bis*(4-(4-(didodecyl-amino)styryl)benzylidene)cyclopentan-1-one (BZC9) and 2,6-*bis*(4-(4-(didodecylamino) styryl)benzylidene)-4-methylcyclohexan-1-one (BZC10) in which an increase of the size of the middle ring was observed. Blue-shift of the absorption maxima upon increase of the middle size ring is consistent with previous results reported in the literature.[332] Indeed, increase of the carbon number in the central ring results in major changes in geometry, strongly affecting the conjugation and thus the position of the absorption maxima. Replacement of the double bond in BZC10 by a triple bond in 2,5-*bis*(4-((4-(dihexylamino)phenyl)ethynyl) benzylidene)cyclopentan-1-one (BZC11) only slightly modified the position of the absorption maximum (444 nm for BZC10 vs. 440 nm for BZC11), but nevertheless blue-shifted the absorption maximum by ca. 4 nm (See Figure 13). Blueshift of the absorption maximum for BZC11 compared to BZC10 was assigned to a triple bond less polarizable than a double bond.[360] This point was confirmed during the solvatochromic studies, which evidenced a positive solvatochromism for all dyes. Fluorescence experiments also demonstrated a severe reduction of the photoluminescence quantum yield upon increase of the middle ring size, resulting from a greater movement flexibility and favoring nonradiative relaxation pathways of the excited states. Jointly, a decrease of the fluorescence lifetimes upon increase of the middle ring size was evidenced, indicating faster nonradiative decays of the excited states upon increase of the flexibility. Thus, in toluene, fluorescence decay measurements revealed the excited state lifetime of BZC8 to be of 1.93 ns, decreasing to 0.68 ns for the more flexible compound BZC10.

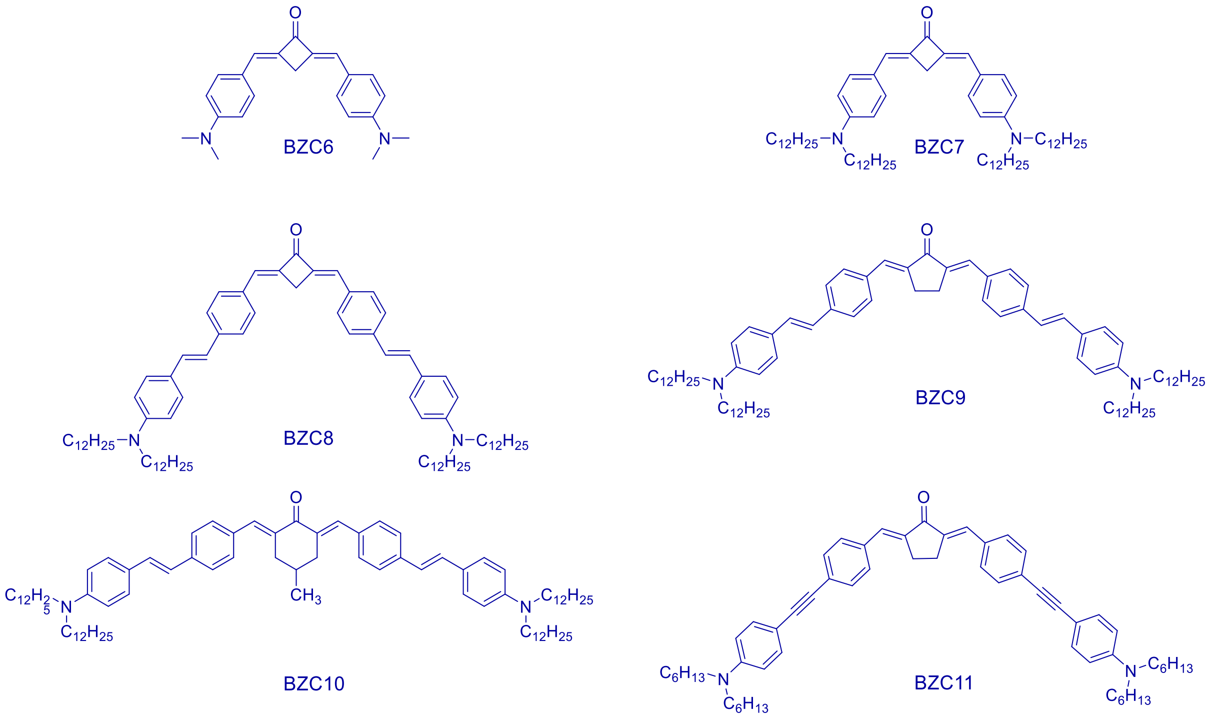


Figure 12. Chemical structures of benzylidene ketones BZC6-BZC11 investigated by Gryko and coworkers.

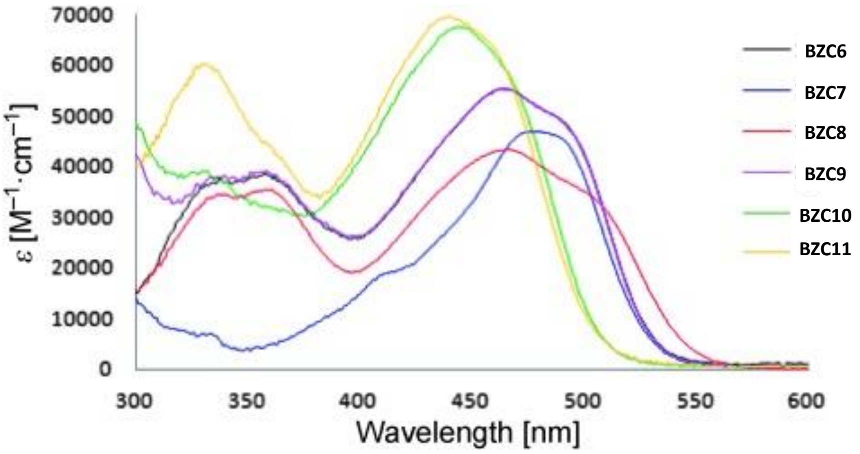


Figure 13. UV-visible absorption spectra of compounds BZC6-BZC11 in toluene. Reproduced with permission of Ref.[359]

Two-photon absorption cross sections determined by Z-scan measurements at 800 nm confirmed the trend determined by other authors. Thus, upon elongation of the π-conjugated system, an enhancement of the two-photon absorption cross section was determined. Among the most interesting findings, increase of the middle ring size increased the two-photon absorption cross section from 50 GM for the four-membered ring BZC8 to 130 and 200 GM for compounds BZC9 and BZC10. By replacing the double bond in BZC9 by a triple bond in BZC11, a threefold increase of the two-photon absorption cross section could be determined, increasing from 130 GM for BZC9 up to 370 GM for BZC11. Interestingly, elongation of the alkyl chain length also contributed to enhance the two-photon absorption cross section. Thus, if a value of 70 GM was determined for BZC9, this value increased by a factor 2 for BZC10 (140

GM). Noticeably, the two-photon absorption spectra of the different dyes exhibited two bands, ascribed to the S_0–S_1 and S_0–S_2 transitions.[361–363] In order to use the different dyes as two-photon initiators, the fabrication window corresponding to the power difference between the polymerization threshold and the burning threshold was determined. As shown in the Figure 14, the broadest fabrication windows were determined for compounds BZC9 and BZC11, bearing a central five-membered ring. Elongation of the π-conjugation decrease the polymerization threshold from 15 mW for compound BZC6 to 5 mW for BZC9-BZC11. Among dyes displaying an elongated structure, BZC10 exhibited the lowest burning threshold, what was assigned to its low yield of photofragmentation into radicals.

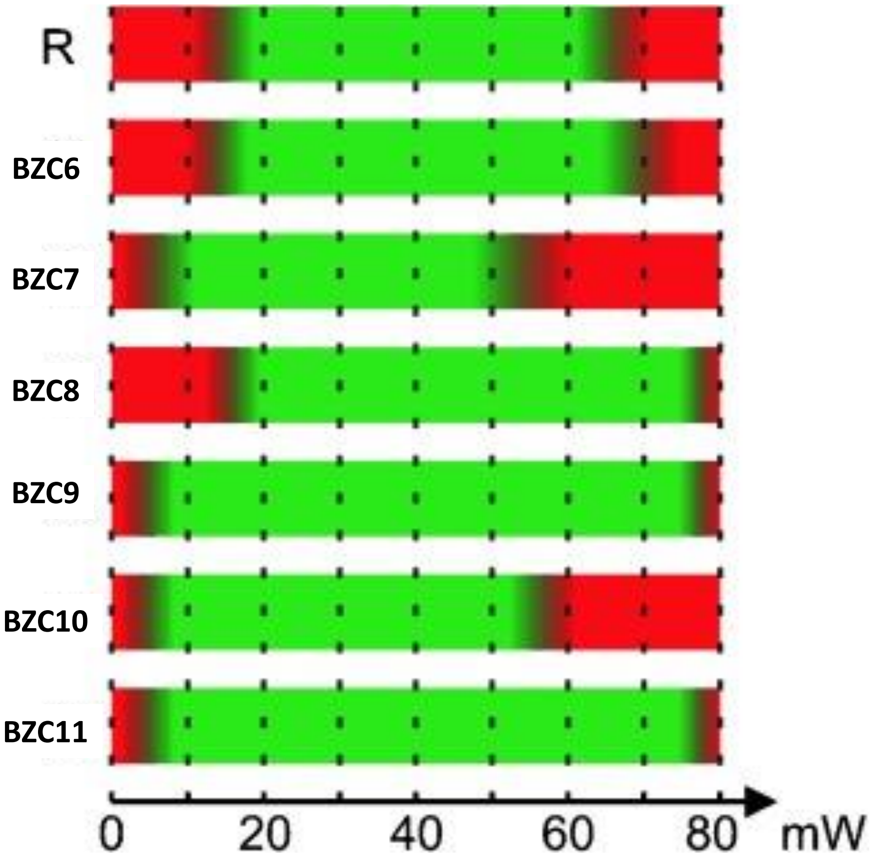


Figure 14. Fabrication window (FW) determined for the different dyes BZC6-BZC11 and the reference compound R (4,4'-*bis*(diethylamino)benzophenone). Reproduced with permission of Ref.[359]

Finally, ability of BZC6-BZC11 to behave as two-photon initiators was demonstrated by elaborating 2D and 3D pattern with BZC11 exhibiting the highest two-photon absorption cross section. As shown in the Figure 15, 2D and 3D patterns with an excellent spatial resolution could be obtained, excepted at the polymerization threshold for which distorted structures due to incomplete polymerizations were obtained.

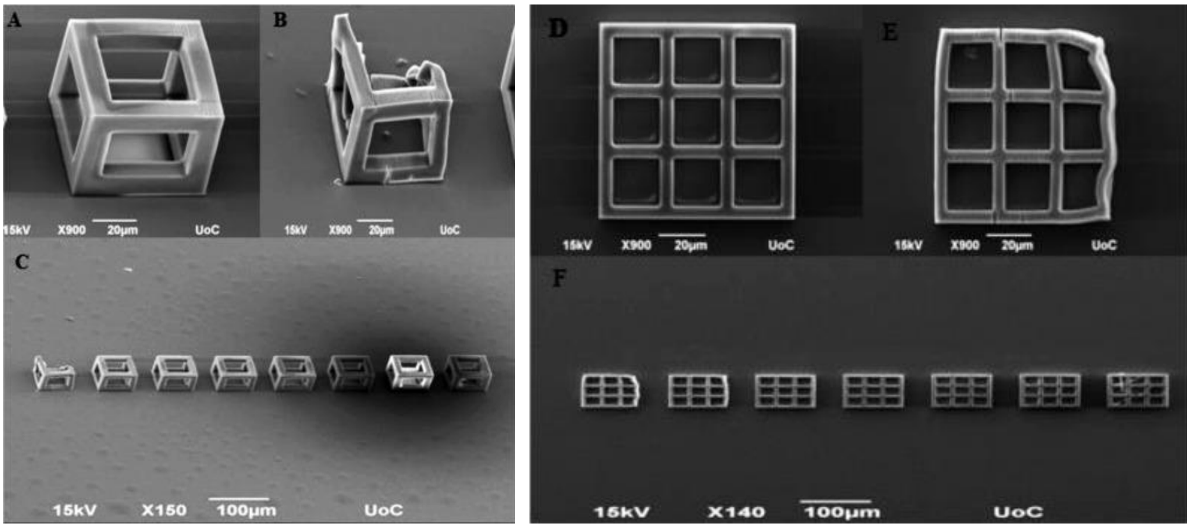


Figure 15. 2D and 3D patterns obtained by two-photon polymerization using BZC11 as initiator. Reproduced with permission of Ref.[359]

Considering that an expansion of the π-conjugation is beneficial to get a broad two-photon polymerization window, a series of benzylidene ketones varying by the middle ring size and possessing peripheral coumarins were proposed by Gryko and coworkers.[364] A series of 4 coumarin-based structures was proposed and their photoinitiating abilities were compared to that of two references compounds, namely 7-(didodecylamino)-2-oxo-2*H*-chromene-3-carbaldehyde (M) and 4,4′-diethylaminobenzophenone (R) (See Figure 15). Biocompatibility of photoinitiators was also examined in this work. Choice of coumarins as peripheral groups was notably motivated by the remarkable photoinitiating ability of these dyes in one-photon polymerization[97–108,365–367] and two-photon polymerization.[368–371] Examination of the UV-visible absorption properties in toluene of 3,3'-carbonyl*bis*(7-(dihexylamino)-2*H*-chromen-2-one) (BZC12) and 3,3'-carbonyl*bis*(7-(didodecylamino)-2*H*-chromen-2-one) (BZC13) revealed the two dyes to absorb at 477 and 475 nm respectively (See Table 1). By replacing the five-membered ring of 3,3'-((2-oxocyclopentane-1,3-diylidene)*bis*(methanylylidene))*bis*(7-(didodecylamino)-2*H*-chromen-2-one) (BZC14) by a six-membered ring in 3,3'-((5-methyl-2-oxocyclohexane-1,3-diylidene)*bis*(methanylylidene))*bis*(7-(didodecylamino)-2*H*-chromen-2-one) (BZC14), a blue-shift of the absorption maxima (540 and 514 nm for BZC14 and BZC15 respectively), consistent with previous results reported in the literature mentioning the presence of internal torsion adversely affecting the electronic delocalization. For comparison, absorption of the parent 7-(didodecylamino)-2-oxo-2*H*-chromene-3-carbaldehyde (M) was only located at 462 nm in toluene. Absorption maxima of all dyes shifted bathochromically in dichloromethane, from 10 nm for M to 25 nm for compounds BZC14 and BZC15. Very short excited state lifetimes were also determined for all dyes, ranging from 0.05 ns for BZC12 and BZC13 to 0.9 and 0.07 ns for BZC14 and BZC15. A severe reduction of the excited state lifetimes was determined for the *bis*-coumarins BZC14/BZC15 compared to that of M (1.95 ns).

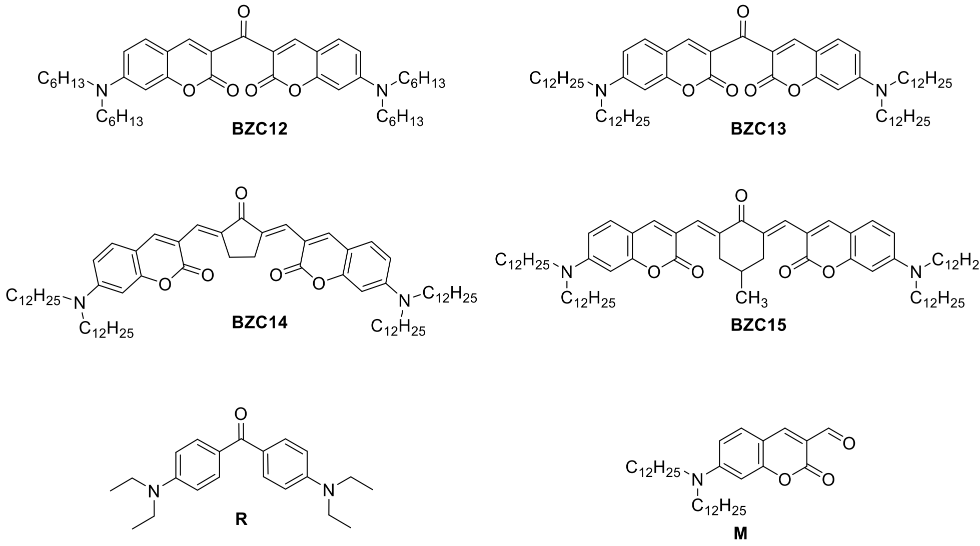


Figure 15. Chemical structures of photoinitiators investigated by Gryko and coworkers.[364]

Table 1. Photophysical properties of the 4 coumarin-based photoinitiators investigated by Gryko and coworkers.[364]

Compounds	λ_{max} (nm)	ε (M^{-1}. cm^{-1})	λ_{em} (nm)	ϕ_{fl}	τ (ns)
BZC12	451	89700	477	0.010	0.05
BZC13	450	91000	475	0.010	0.05
BZC14	479, 504	55100, 57900	540, 578 (sh)	0.251	0.90
BZC15	460	72100	514, 558 (sh)	0.025	0.07
M	440	52700	462	0.576	1.95

Determination of the fabrication window consisting in the determination of the difference existing between the lower polymerization threshold and the higher burning threshold revealed BZC14 and BZC15 to exhibit a fabrication window shifted at higher energies compared to BZC12 or BZC13 also being *bis*-coumarin structures but not benzylidene ketones (See Figure 16). A good correlation between two-photon absorption cross-section and fabrication window was determined. Finally, examination of the morphology of preosteoblastic cells cultured on polymers elaborated with BZC12, BZC13, BZC14 and BZC15 revealed the development of preosteoblastic cells to be comparable to that of the reference culture done on polystyrene. Especially, all cells displayed a similar elongated morphology and the number of cells on the different examined surfaces were identical, indicating a comparable growth rate of cells.

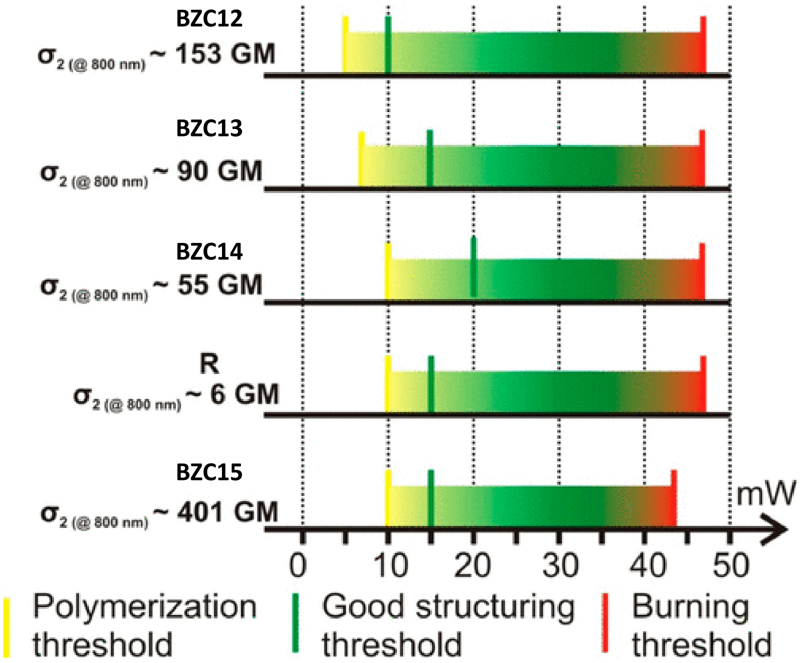


Figure 16. Two-photon absorption cross-sections, fabrication window, and threshold values of different photoinitiators BZC12-BZC15. Reproduced with permission of Ref. [364]

Finally, in 2021, a series of 12 benzylidene cyclopentanones varying by the peripheral groups was proposed as efficient photoinitiators for 3D printing applications by Lalevée and coworkers (See Figure 17).[176] As interesting features, upon introduction of a silver salt, silver nanoparticles could be generated during the polymerization process. As shown in the Figure 18 and in the Table 2, all dyes showed a significant absorption in the visible range so that polymerization experiments could be carried out at 405 and 470 nm. Noticeably, the most red-shifted absorptions were found for BZC2, BZC21 and BZC26, absorption peaking respectively at 460, 485 and 460 nm. All these dyes comprise dialkylaminobenzene or diphenylaminobenzene moieties as peripheral groups. Conversely, for the other dyes, absorption maxima below 460 nm were determined in acetonitrile, consistent with the presence of weaker electron donating groups (See Figure 18 and Table 2).

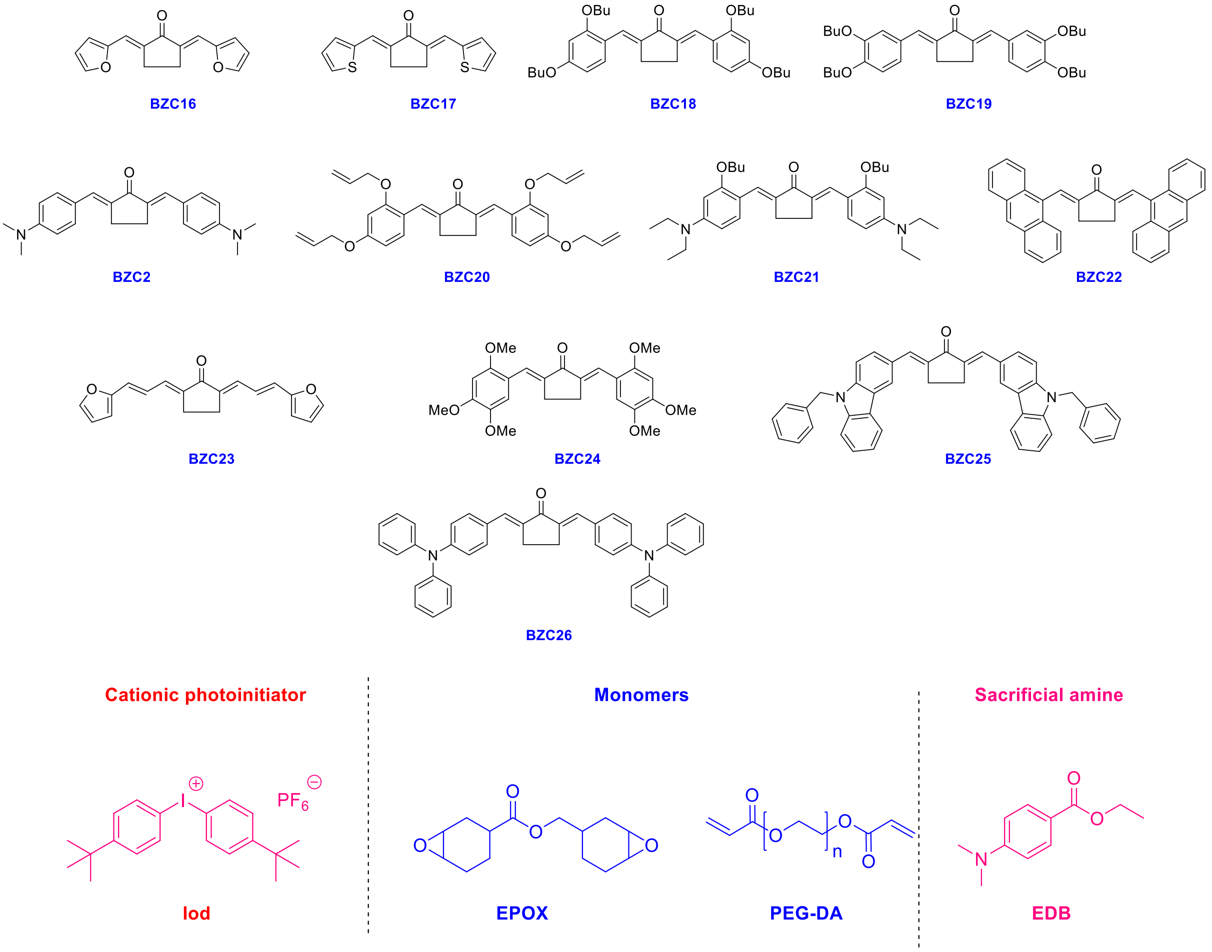


Figure 17. Benzylidene cyclopentanones BZC2, BZC16-BZC26 examined by Lalevée and coworkers as one-photon photoinitiators.

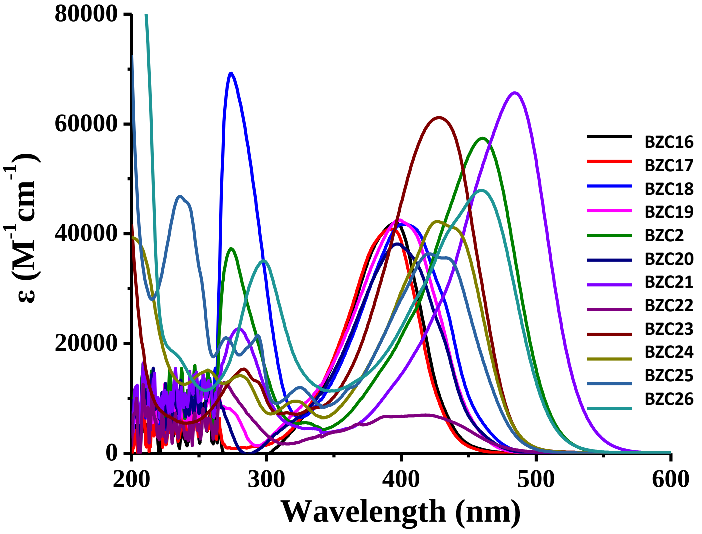


Figure 18. UV-visible absorption spectra of BZC2, BZC16-BZC26 in acetonitrile. Reproduced with permission from Ref.[176]

Table 2. Light absorption properties of BZC2, BZC16-BZC26 in acetonitrile: maximum absorption wavelengths λ_{max}; extinction coefficients at λ_{max} (ε_{max}) and extinction coefficients at the emission wavelength of the LED@405 nm ($\varepsilon_{@405nm}$) and LED@470 nm ($\varepsilon_{@470nm}$).

Chalcones	λ_{max} (nm)	ε_{max} ($M^{-1}.cm^{-1}$)	$\varepsilon_{@405nm}$ ($M^{-1}.cm^{-1}$)	$\varepsilon_{@470nm}$ ($M^{-1}.cm^{-1}$)
BZC16	396	41 980	37 050	270
BZC17	392	40 840	33 590	110
BZC18	400 274	41 770 69 250	41 610	2720
BZC19	399	42 500	41 580	1280
BZC2	460 274	57 400 37 300	23 700	53 446
BZC20	397	38 150	36 700	1710
BZC21	485 278	65 670 22 680	16 200	59 370
BZC22	418 268	6970 12 890	6800	1600
BZC23	428 283	61 130 15 340	50 310	16 540
BZC24	427 280	42 062 14 160	32 270	14 380
BZC25	421 236	36 350 46 810	30 560	10 160
BZC26	460 298	47 620 35 060	25 300	44 400

Photoinitiation abilities of the different dyes were examined during the free radical polymerization (FRP) of PEGDA in three-component dye/Iod/amine (0.1/1.5/1.5 wt%) photoinitiating system upon irradiation at 405 and 470 nm in thin and thick films (See Table 3). Compared to the reference two-component Iod/amine combination furnishing a final monomer conversion of 76% after 200 s of irradiation at 405 nm in thin films, all dyes in three-component systems could provide monomer conversions on par or even higher than that of the two-component Iod/amine system. It therefore demonstrated the crucial role of the different dyes during the initiating step. Remarkably, BZC17, BZC18, BZC22 and BZC23 could even furnish double bond conversion higher than 90 wt% within 50 s, evidencing the reactivity of these three-component systems. In thick films, a reduction of the monomer conversion was observed for all dyes, excepted for BZC2 for which a significant enhancement of the monomer conversion was observed. Surprisingly, the three-component system based on BZC2 could even outperform the reference system (92% conversion for BZC2 vs. 87% for the reference system). Reduction of the monomer conversion in thick films was assigned to inner filter effects, impeding light penetration within the photocurable resin. Conversely, photoinitiating ability of the iodonium/amine combination at 405 nm was assigned to the formation of a charge transfer complex absorbing at this wavelength.[372] At 470 nm, considering that the iodonium/amine combination does not absorb anymore, all three-component photoinitiating systems became interesting combinations since activable at wavelengths where the reference system doesn't operate anymore. Besides, a reduction of the monomer conversion was observed both in thin or thick films and these differences of reactivity were determined as originating from their molar extinction coefficients at 470 nm. In the case of BZC2, an improvement of the monomer conversion was observed in thick films compared to thin film whereas the opposite trend was found for all the other dyes. The unusual behavior of BZC2 could not be rationalized by the authors. Indeed, reactivity of dyes in photopolymerization results from a subtle interplay between molar extinction coefficient, solubility of the dyes in resins, rate constants of interaction with the different additives and excited state lifetimes.

Table 3. Final monomer conversions determined during the FRP of PEGDA using three-component dye/Iod/amine photoinitiating systems in thin and thick films upon irradiation with LEDs emitting at 405 or 470 nm. The blank corresponds to the two-component Iod/amine system.

Final double bond conversions (FC) initiated by dye/Iod/amine				
Dyes	LED@405nm		LED@470nm	
	Thickness~20µm	Thickness~2mm	Thickness~20µm	Thickness~2mm
BZC16	76%	7%	40%	n.p.
BZC17	93%	n.p.	31%	n.p.
BZC18	96%	70%	39%	40%
BZC19	80%	30%	89%	70%
BZC2	73%	92%	70%	90%
BZC20	83%	n.p.	65%	50%
BZC21	75%	70%	68%	70%
BZC22	92%	n.p.	5%	n.p.
BZC23	90%	13%	63%	n.p.
BZC24	75%	62%	76%	88%
BZC25	76%	62%	84%	57%
BZC26	79%	25%	86%	30%
Blank	76%	87%	n.p.	n.p.

n.p. no polymerization.

Noticeably, photoinitiating ability of benzylidene cyclopentanones was not limited to the FRP of acrylate but also extended to the cationic polymerization of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EPOX), what is relatively unusual for benzylidene ketones. As shown in the Table 4, even if all three-component dye/Iod/amine (0.1/1.5/1.5 wt%) photoinitiating systems could initiate the CP of EPOX, monomer conversions remained lower than that obtained with the reference system, excepted for BZC20 that could outperform the reference system in thin films. Irrespective of the photoinitiating system, no polymerization of EPOX could be obtained in thick films due to inner filter effects. Difference of reactivity between the different dyes is directly related to the photochemical reactivity of the different dyes towards the amine or the iodonium salt and the ability to facilely generate dye$^{\bullet+}$ radical cations. Photolysis experiments done in acetonitrile with the two-component dye/Iod and dye/amine systems and the three-component dye/Iod/amine systems revealed the different dyes to interact more efficiently with the iodonium salt than with the sacrificial amine. Theoretical feasibility of the interactions between the different dyes and the two additives (Iod or amine) was also investigated by determining the free energy changes (ΔE) of the electron transfer reactions. In the two cases, negative free energy changes were determined, evidencing the feasibility of the electron transfer between the dye and the two additives. By electron spin resonance (ESR)-spin trapping experiments, formation of aryl radicals by use of the three-component photoinitiating systems was demonstrated, thus proving the occurrence of an interaction between the different dyes and Iod. Interestingly, upon introduction of silver nitrate into the photocurable resins, part of the initiating radicals could be used to convert silver cations as silver (0) and thus the formation of Ag nanoparticles (AgNPs). As shown in the Figure 19, presence of silver nanoparticles within the polymer films was demonstrated by optical microscopy. As specificities, nanoparticles of different sizes and shapes can be found throughout the whole polymer. In most of the cases, aggregates of nanoparticles were found. On the opposite, silver nanoparticles prepared in DMF with the same three-component system are monodisperse and of small and regular sizes.

Table 4. Final monomer conversions obtained during the cationic polymerization of EPOX using the three-component dye/Iod/amine system for thin films upon irradiation with a LED emitting at 405 nm.

Final EPOX conversions (FCs) obtained with the three-component dye/Iod/amine systems							
Dyes	**BZC16**	**BZC17**	**BZC18**	**BZC19**	**BZC2**	**BZC20**	**BZC21**
FCs	50%	48%	70%	46%	72%	92%	65%
Dyes	**BZC22**	**BZC23**	**BZC24**	**BZC25**	**BZC26**	**Blank**	
FCs	46%	45%	46%	69%	73%	77%	

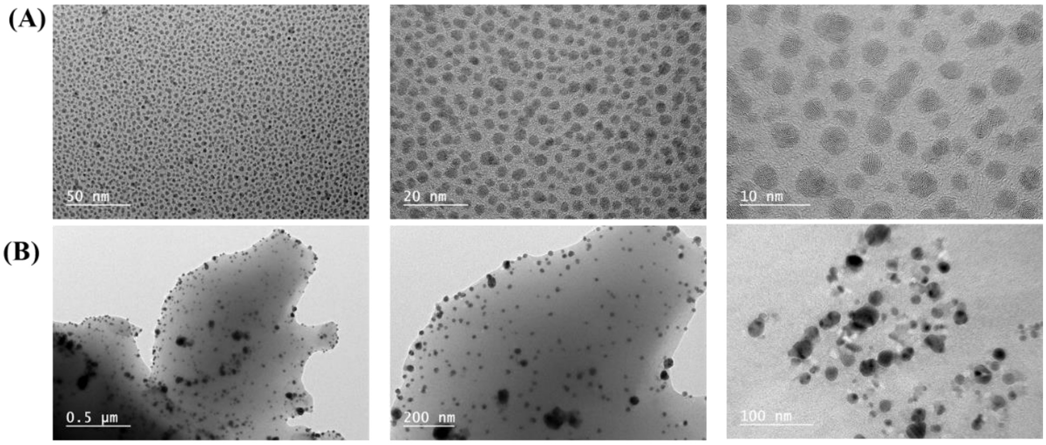


Figure 19. TEM images of (A) AgNPs prepared in DMF solution; (B) AgNPs prepared in PEG-polymer during photopolymerization. Reproduced with permission from Ref.[176]

To support the formation of silver nanoparticles, the mechanism depicted in the Figure 20 was proposed. Due to the presence of an oxidative and a reductive pathway, three different families of radicals Ar•, EDB• and dye-H• are formed and can be used as reducing agents for silver nitrate.

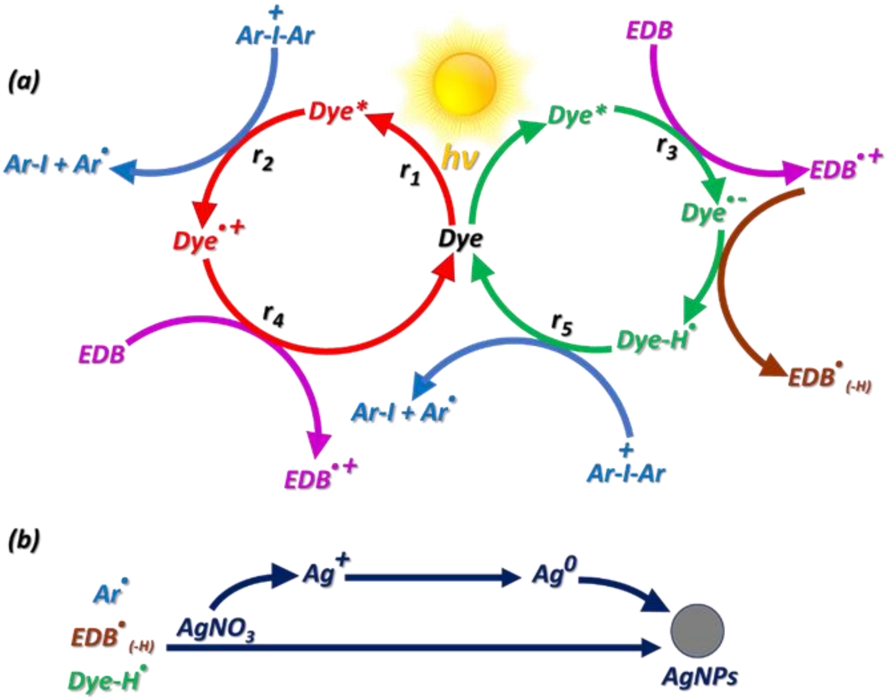


Figure 20. Mechanism involved in the polymerization of PEGDA and the formation of silver nanoparticles. Reproduced with permission from Ref.[176]

Examination of the swelling properties of PEGDA films revealed the presence of Ag nanoparticles to drastically reduce the ability of polymers to absorb light, consistent with part of the interchain spaces occupied by Ag nanoparticles. Reversibility of the water swelling process was also demonstrated. Finally, considering that PEGDA-based polymers could be reversibly hydrated and dehydrated, these photoinitiating systems were thus investigated for 4D printing applications and thus the design of shape memory objects. 4D printing consists in elaborating objects by 3D printing whose shapes can be modified by mean of external stimuli.[43,373–376] In the present case, heat and water were selected as the two stimuli capable to modify the shape of PEGDA-based objects. As shown in the Figure 21 for a cross printed using the BZC2-based three-component photoinitiating system and of 1 mm thick, immersion of the cross during one hour could modify the shape of the cross, consistent with the hydration of PEGDA polymer. Upon heating at 100°C for 100 s, the cross could return to its initial shape. Noticeably, by maintaining the heating for 10 min., an inversion of the curvature of the cross was observed, resulting from the complete dehydration of the PEGDA polymer in forced conditions. Finally, at ambient temperature, the cross could return to its initial shape. Repeatability of this four-step cycle (hydration, dehydration, inversion of curvature, return to the initial shape) was verified by cycling several times. Noticeably, comparisons between the polymers containing or not Ag nanoparticles revealed the curvature of Ag-based polymers to be lower than that of the polymer films without Ag particles, consistent with the results obtained during the swelling experiments. Notably, presence of Ag nanoparticles impedes water penetration within the polymer.

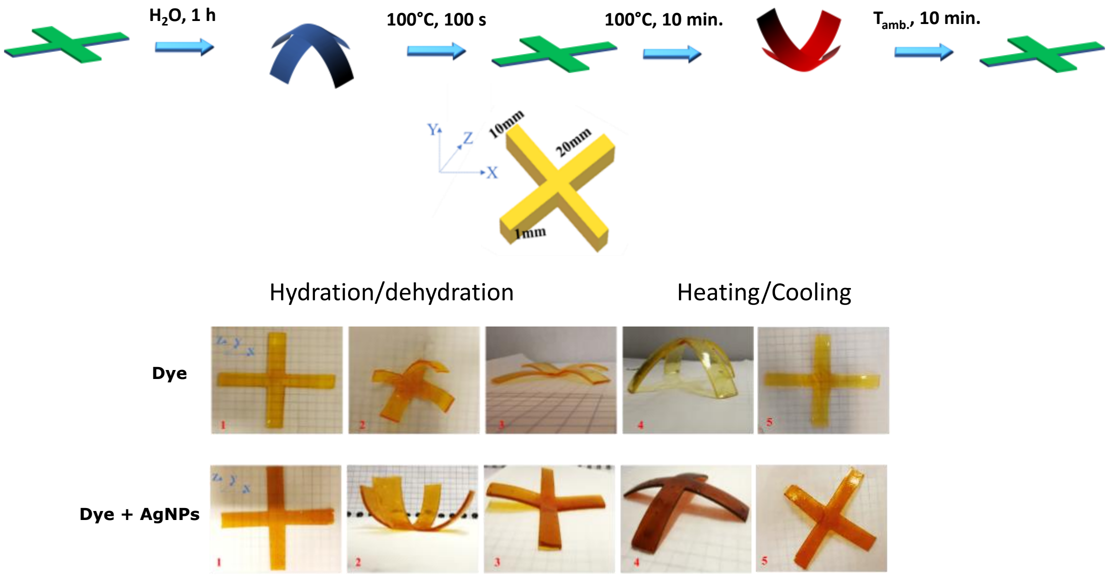


Figure 21. Investigations of PEGDA films prepared with BZC2 in 4D printing applications. Different pictures evidencing the shape memory effect. Reproduced with permission from Ref.[176]

Water solubility of photoinitiators is a major issue as it could allow the polymerization in water, and thus the development of polymerization processes more respectful from the environment. In 2009, a benzylidene cyclopentanone was chemically modified so that the introduction of four water-soluble chains could be possible (See Figure 22).[377] Due to the presence of four carboxylate groups, 2,5-*bis*-{4-[*bis*-(2-sodiumcarboxylate-ethyl)-amino]-benzylidene}-cyclopentanone (BSEA) showed a good solubility in water. As drawback, a severe reduction of the two-photon absorption cross-section of 287 GM at 800 nm (determined by NLT method) was found for BSEA in water, far from the value of 607 GM obtained in DMF for the water-insoluble BDEA. This unexpected behavior was assigned to an aggregation of the molecules in water, a structural distortion of the molecule or the formation of hydrogen bonds between the electron-donating groups of BSEA and water adversely affecting its two-photon absorption cross-section.[378–380] Besides, this value remains higher than that determined for P2CK, a two-photon absorption cross-section of 176 GM being determined at 800 nm in water.[381,382] It has to be noticed that P2CK was nonetheless used for photopolymerization experiments but also for one- and two-photon excited photodynamic therapy (TPE-PDT), demonstrating the versatility of this structure.[383]

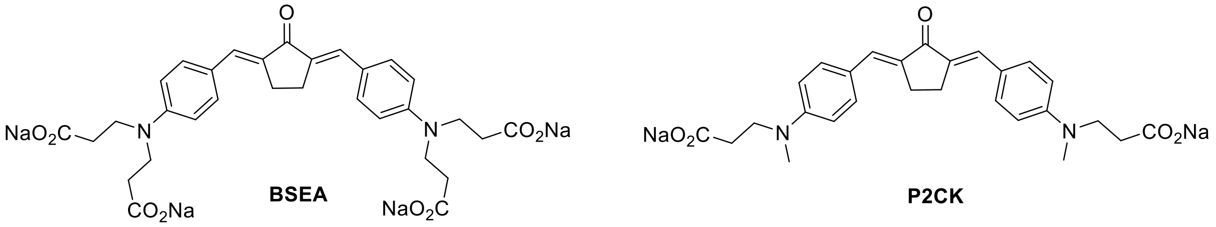


Figure 22. Chemical structure of BSEA and P2CK.

Recently, BSEA was revisited in a more extended study aiming one again at investigating the influence of the middle ring size on the two-photon absorption properties of benzylidene ketones (See Figure 23).[297] Here again, crucial importance of the middle ring size was evidenced. Thus, if an increase of the two-photon absorption cross-section from 567 (T1) to 808 GM (BSEA) was determined in deionized water, this value decreased to 231 GM for the six-membered ring T3. It has to be noticed that the two-photon absorption cross-section of BSEA determined in this work strongly differs from the value obtained in the previous work (297 GM determined by NLT method vs. 808 GM for BSEA determined by 2PEF method in this work and in the same solvent i.e. water). Meanwhile, if different, comparison between T1, BSEA and T3 remains possible, the three values being determined in the same conditions. Considering that the two-photon absorption cross-section is strongly dependent on the intramolecular charge transfer, the low TPA cross-section of T3 was assigned to the flexibility of the six-membered ring in T3, distorting the structures and reducing the electronic delocalization.

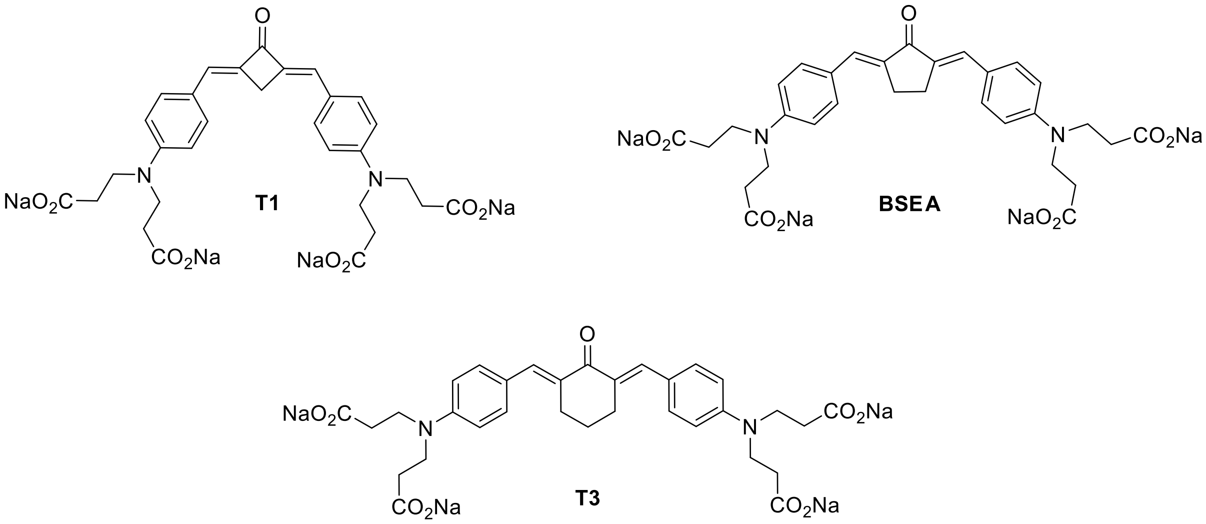


Figure 23. Chemical structures of **T1, BSEA** and **T3**.

In 2020, an elegant strategy was developed by Nie and coworkers to produce water soluble photoinitiators.[384] Instead of modifying a photoinitiator by mean of chemical engineering in order to introduce water-soluble groups, Nie and coworkers used triethanolamine (TEOA) as an electron donor to form an intermolecular charge transfer with the water-insoluble 2,6-*bis*(furan-2-ylmethylidene)cyclohexan-1-one (BFC) (See Figure 24). Using this strategy, one-photon polymerization of PEGDA could be carried out while using 2 wt% BFC/TEOA charge transfer complex (CTC), even if a water solubility up to 5 wt% for the BFC/TEOA CTC was determined. Parallel to this, an extended absorption of the CTC compared to that of BFC in the visible light region was also demonstrated. Thus, a redshift of the absorption maximum was found from 373 nm for BFC to 400 nm for the BFC/TEOA CTC (See Figure 25). This redshift was also evidenced during the photoluminescence experiments. Thus, if emission maximum of BFC was located at 483 nm, this value shifted to 578 nm for BFC/TEOA CTC in acetonitrile.

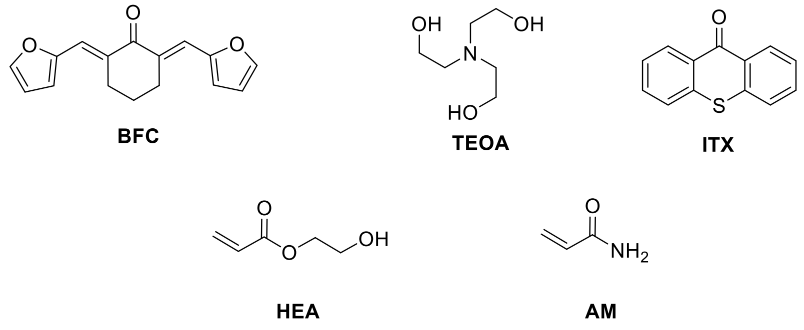


Figure 24. Chemical structure of BFC, different monomers and additives.

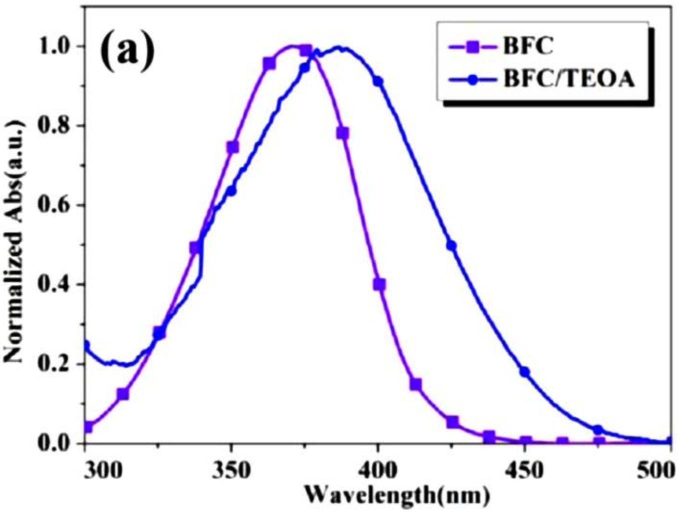


Figure 25. UV-visible absorption spectra of BFC and BFC-TEOA CTC in acetonitrile. Reproduced with permission of Ref.[384]

Examination of the photoinitiating abilities revealed a significant enhancement of the monomer conversion upon increase of the BFC/TEOA CTC concentration upon irradiation at 405 nm with a LED (See Figure 26). Thus, the final monomer conversion of acrylamide (AM) increased from 38% up to 80% by increasing the CTC concentration from 0.5 to 3 wt%. This trend was confirmed during the FRP of poly(ethylene glycol)diacrylate (PEGDA) or hydroxyethyl acrylate (HEA).

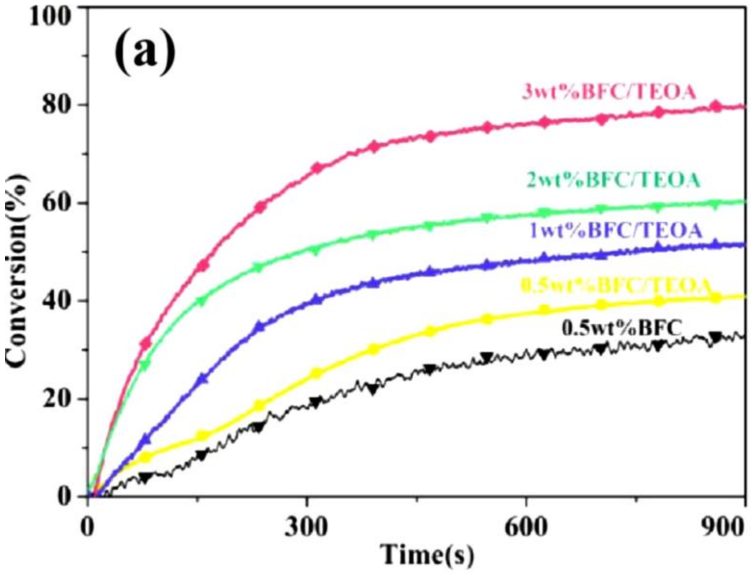


Figure 26. Photopolymerization profiles determined during the FRP of acrylamide (AM) using BFC (0.5 wt%), BFC/TEOA (0.5 wt%), BFC/TEOA (1 wt%), BFC/TEOA (2 wt%), BFC/TEOA (3 wt%) during the FRP of AM upon irradiation with a LED 405 nm (I = 70 mW/cm^2). Reproduced with permission of Ref.[384]

Finally, a mechanism supporting the polymerization process was proposed by the authors (See Figure 27). After formation of the charge transfer complex, upon photoexcitation, an electron transfer can occur from the electron-donating TEOA to the electron-accepting BFC. Subsequently to this first step, a hydrogen abstraction by the ketone can occur, generating α-aminoalkyl radicals capable to initiate free radical polymerizations (See Figure 27).

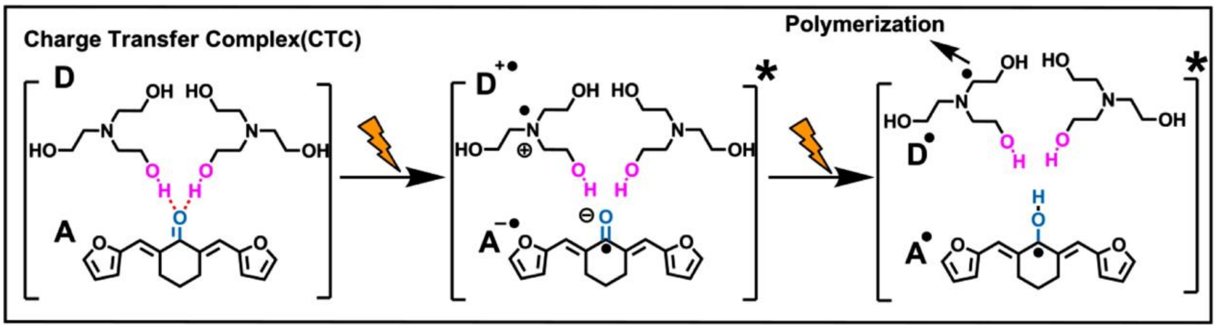


Figure 27. Mechanism involved during the FRP initiated by the BFC/TEOA CTC. Reproduced with permission of Ref.[384]

3. Asymmetrically substituted benzylidene cyclopentanones

Symmetrically substituted cyclopentanones were not the only structures to be studied as one and two-photon photoinitiators. Asymmetrically structures were also the focus of several studies. The first one was reported in 2006 by Fang and coworkers.[356] In this pioneering work, three dyes comprising a triphenylamine unit was designed and synthesized. Determination of the two-photon absorption cross-sections of the three dyes revealed 5,5',5''-((nitrilotris(benzene-4,1-diyl))*tris*(methanylylidene))*tris*(2-((E)-4-(dimethylamino) benzylidene)cyclopentan-1-one) (BZC29) to exhibit a two-photon absorption cross-section of 3298 GM which is six times higher than that of the reference compound i.e. BZC2.

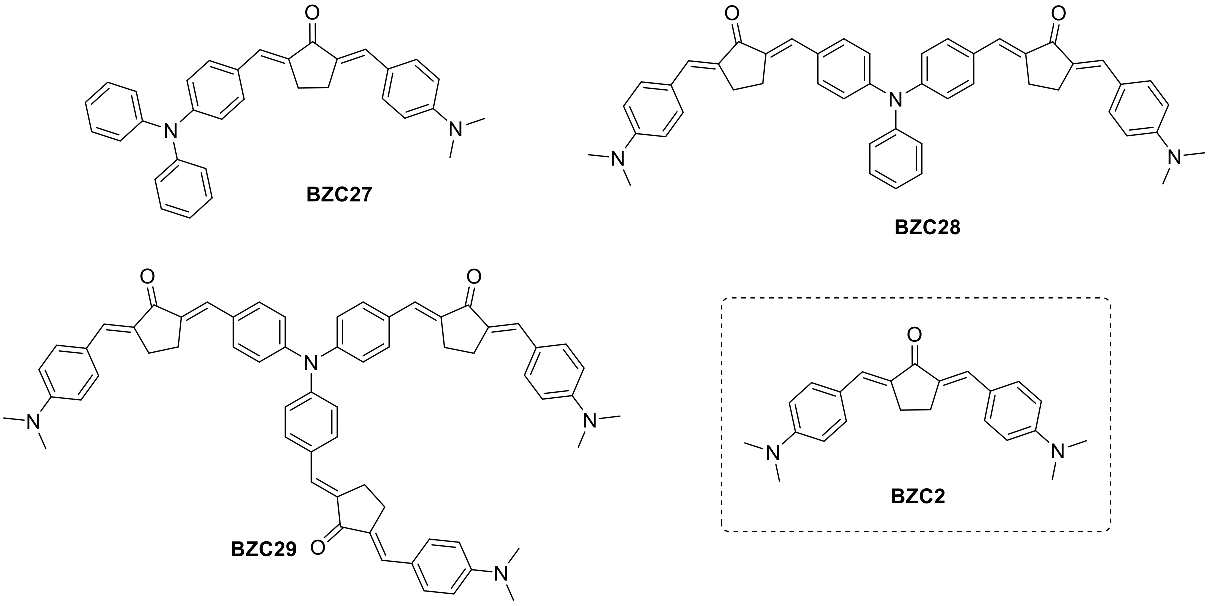


Figure 28. Chemical structures of multibranched triphenylamine-based dyes BZC27-BZC29 and the reference compound BZC2.

Investigations of their UV-visible absorption properties in chloroform revealed the absorption maxima of the three dyes to be located at 470, 490 and 492 nm for BZC27-BZC29 respectively. A redshift of the absorption maximum was found upon increase of the number of branches even if only a slight shift was observed between BZC28 and BZC29, evidencing the limitation of this approach (See Figure 29). A redshift of the emission was also observed, BZC27-BZC29 emitting at 546, 550 and 552 nm respectively. A decrease of the Stokes shift with the number of branches was observed which may be due to a decrease of the excited-state charge transfer in multibranched structures. Determination of their two-photon absorption cross-sections at 800 nm revealed values of 781, 2474 and 3298 GM, for BZC27-BZC29 respectively. Based on previous results reported in the literature, enhancements of the two-photon absorption cross-section in multibranched compounds was assigned to vibronic coupling and electronic coupling between chains and therefore of cooperative effects.[385,386] However, considering that the enhancement of the two-photon absorption cross-section values decreased with increasing the numbers of branches, electronic coupling between chains was determined as being the main cause of variation of these values. Noticeably, even if the two-photon absorption cross-sections of BZC28 and BZC29 are high, such values have previously been reported in the literature for other structures such as pyrylium,[387] triphenylamine derivatives[388] or 3,5-dicyano-2,4,6-tristyrylpyridine derivatives.[389]

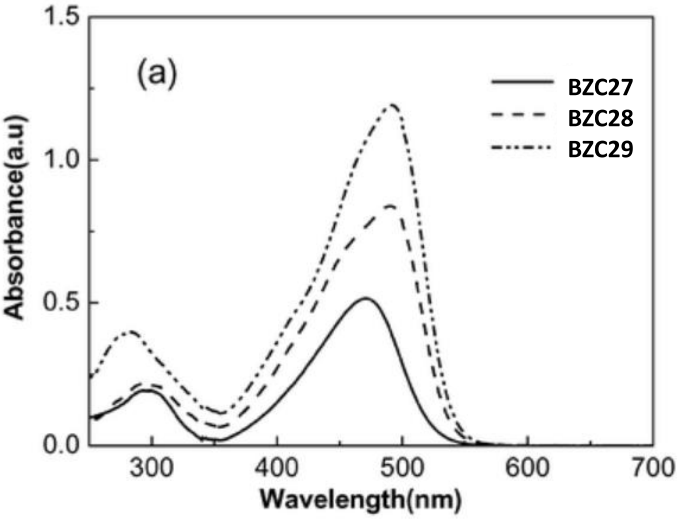


Figure 29. UV-visible absorption spectra of BZC27-BZC29 in chloroform. Reproduced with permission of Ref.[356]

Examination of their photoinitiating abilities in two-component systems with 4,4'-dimethyldiphenyliodonium hexafluorophosphate during the FRP of a mixture of three acrylate monomers i.e. 2-phenoxyethyl acrylate/pentaerythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w) upon irradiation with a light source emitting in the 400-500 nm range revealed the two dyes to furnish monomer conversions of 70% after 15 min. of irradiation. Conversely, conversions of only 52 and 60% were obtained with BZC2 and BZC27. Considering the similarity of monomer conversions obtained with BZC28 and BZC29 and their differences of molar extinction coefficients, presence of an inner filter effect for BZC29 adversely affecting its photoinitiating ability during photopolymerization was suggested by the authors as a plausible explanation (See Figure 30).

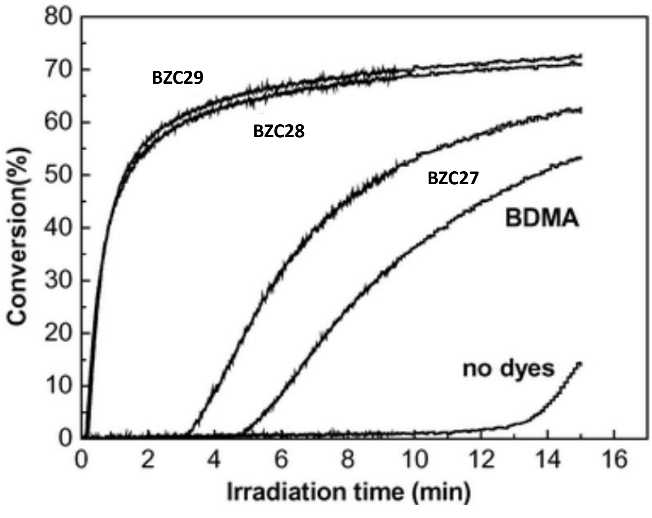


Figure 30. Polymerization profiles determined for BZC27-BZC29 during the FRP of a mixture of three monomers i.e. 2-phenoxyethyl acrylate/pentaerythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w) upon irradiation with a light source emitting in the 400-500 nm range. Reproduced with permission of Ref.[356]

In 2008, five asymmetrically substituted benzylidene cyclopentanones were proposed by Wu and coworkers.[390] In this series of dyes, even if all benzylidene cyclopentanones were designed with electron-donating dialkylaminophenyl groups, in the case of BZC30-BZC34, alkyl chains of different lengths were also introduced on one side, enabling to finely tune the solubility of dyes in resins but also the electron donating ability of this group.

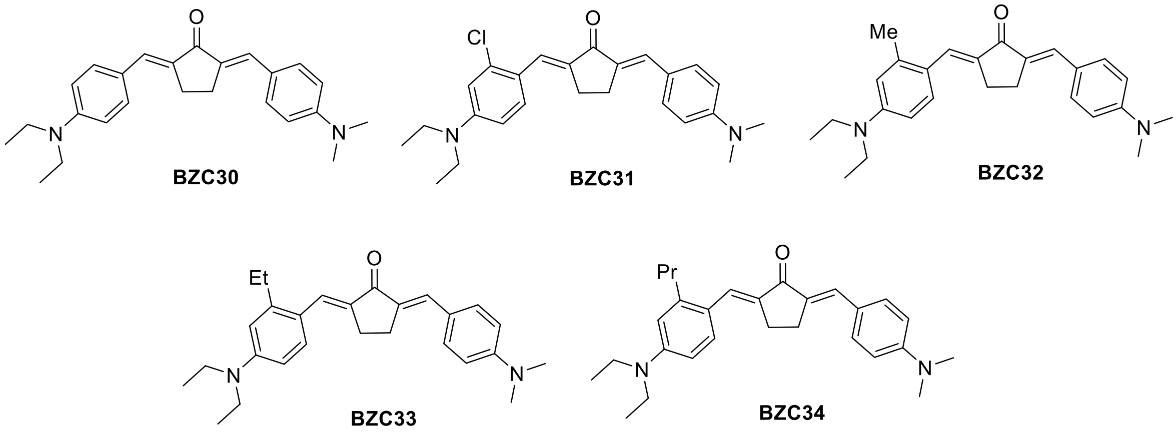


Figure 31. Chemical structures of asymmetrically substituted dyes BZC30-BZC34 proposed by Wu and coworkers.[390]

Compared to the symmetrically substituted benzylidene cyclopentanones depicted in the previous paragraph such as BZC2 or BDEA, no significant modifications of their absorption properties could be found for BZC30-BZC34.[391,392] As shown in the Figure 32, absorption maxima varied between 470 nm for BZC31 to 475 nm for BZC30, BZC33, BZC34 and 477 nm for BZC32 in chloroform. These values are close to that determined for BZC2 and BDEA (λ_{max} = 466 nm) in chloroform.[393] In the case of BZC31, blueshift of the absorption maxima can be assigned to the presence of chlorine atom on one of the dialkylaminophenyl group, adversely affecting its electron-donating ability. Conversely, in the case of BZC32-BZC34, modification of the peripheral chain lengths did not modify the position of the absorption maxima. By using the two-photon excited fluorescence (TPEF) method, TPA cross-sections of BZC30-BZC34 could be determined in chloroform. Values of 506, 510, 386, 466 and 403 GM were respectively determined for BZC30-BZC34. Noticeably, introduction of a lateral alkyl chain adversely affected the TPA cross-section, attributable to its *ortho*-position relative to the double bond so that an internal torsion of the molecule was induced. FRP experiments done for the polymerization of a mixture of three monomers i.e. 2-phenoxyethyl acrylate/pentaerythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w) upon irradiation with a light source emitting at wavelength higher than 470 nm were carried out with two-component systems using hexaarylbiimidazole (HABI) as the co-initiator. As shown in the Figure 33, although the different dyes are of similar structures, major differences could be evidenced during the photopolymerization experiments. Thus, different induction periods and polymerization rates could be detected, evidencing the strong influence of the substitution pattern on the photoinitiating abilities. In this series of dyes, the worse monomer conversion was obtained with the two-component BZC31/HABI combination, once again evidencing the detrimental role of halogen atom on the optical properties and the photoinitiating abilities.

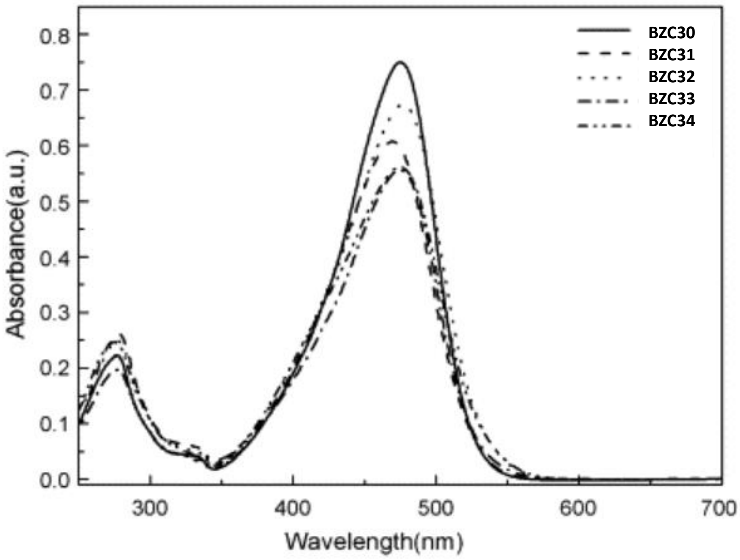


Figure 32. UV-visible absorption spectra of BZC30-BZC34 in chloroform. Reproduced with permission of Ref. [390]

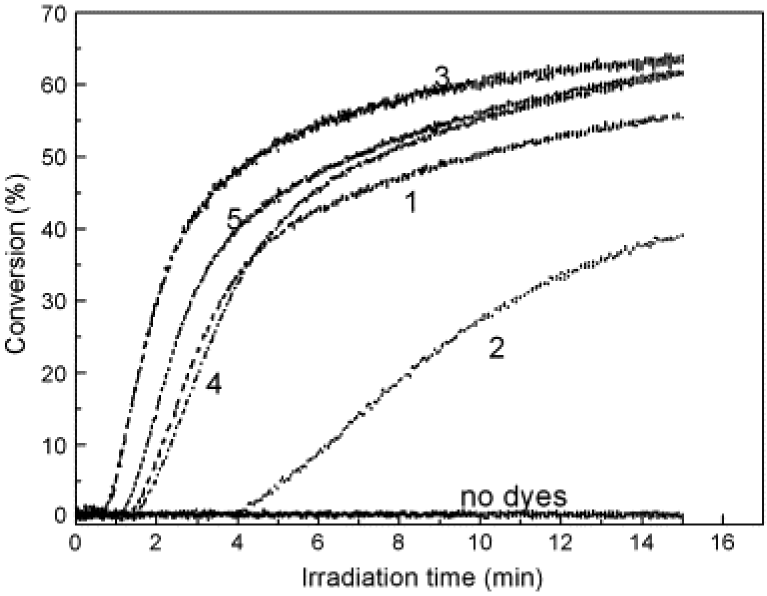


Figure 33. Polymerization profiles determined during the FRP of a mixture of three monomers i.e. 2-phenoxyethyl acrylate/pentaerythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w) upon irradiation with a light source emitting at wavelength higher than 470 nm using BZC30 (1), BZC31 (2), BZC32 (3), BZC33 (4) and BZC34 (5). Reproduced with permission of Ref. [390]

The same year, the same group examined another asymmetrically substituted benzylidene cyclopentanone comprising a coumarin group (See Figure 34).[393] For these two molecules and due to the presence of the coumarin fragment, a significant enhancement of the two-photon absorption cross-sections could be determined in chloroform. Thus, values of 939 and 1150 GM could be respectively determined for BZC35 and BZC36. Compared to BZC2 for which an absorption maximum at 466 nm was found, a significant redshift of the absorption was found for BZC35 and BZC36, peaking at 500 and 521 nm respectively. Compared to the dimethylamino group, the higher electron-donating ability of the coumarin fragment was evidenced. Fluorescence experiments revealed the redshift of the emission maximum to be greater than that of the absorption maximum. Indeed, photoluminescence maxima located at 535, 564 and 580 nm could be determined for BZC2, BZC35 and BZC36. These results demonstrate that the charge transfer character of the main absorption band and the fact that their excited states exhibit a higher polarity than their ground-states. Noticeably, in this study and contrarily to what is done in the other studies, solvatochromism of BZC35 and BZC36 could be rationalized by mean of the Lippert-Mataga solvatochromic semiempirical scale.[394,395] As previously observed for symmetrically substituted benzylidene cyclopentanones, presence of coumarins groups was beneficial to the two-photon absorption cross-section, since values of 939 and 1150 GM at 877 nm were found in chloroform, greatly higher than that of BZC2 (526 GM).

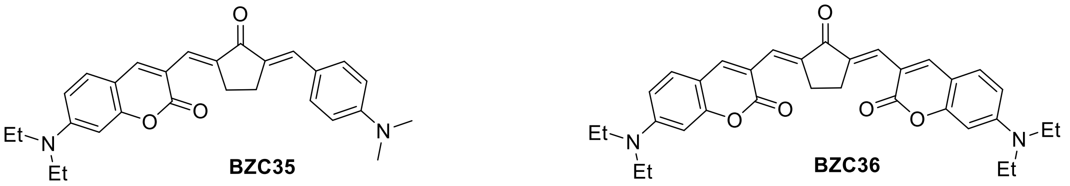


Figure 34. Chemical structures of BZC35 and BZC36.

When tested as photosensitizer for the sensitization of 4,4'-dimethyldiphenyliodonium hexafluorophosphate, an enhancement of the final monomer conversion was observed from BZC2 to BZC35 and BZC36. Thus, conversions of 60, 68 and 70% could be determined after 15 min. of irradiation with a light source emitting in the 400-500 nm range (See Figure 35).

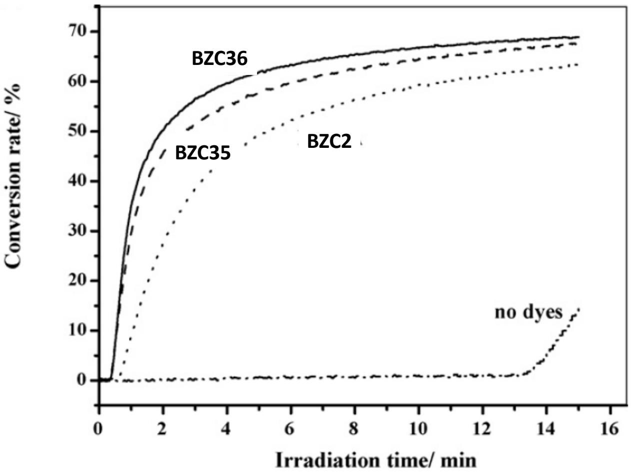


Figure 35. Polymerization profiles determined during the FRP of a mixture of three monomers i.e. 2-phenoxyethyl acrylate/pentaerythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w) upon irradiation with a light source emitting in the 400-500 nm range. Reproduced with permission of Ref. [393]

During the two-photon polymerization experiments, a decrease of the threshold energy was determined upon increase of the dye concentration. Thus, if a threshold of 2.11 mW was determined at 0.01 wt% BZC36 for the polymerization of a mixture of three monomers i.e. 2-phenoxyethyl acrylate/pentaerythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w), this value decreased to 1.05 mW at 0.1 wt%. Upon addition of HABI (1 wt%) and 3-mercapto-4-methyl-1,2,4-triazole (MMT) (1 wt%) as co-initiators, threshold energy could be reduced to 0.44 mW at 1 wt% BZC36. The same burning threshold (3.39 mW) was found irrespective of the additives and the dye used and this burning threshold was assigned to the monomers used for the polymerization experiments. As shown in the Figure 36, 2D and 3D structures could be obtained with a remarkable spatial resolution in the case of BZC36.

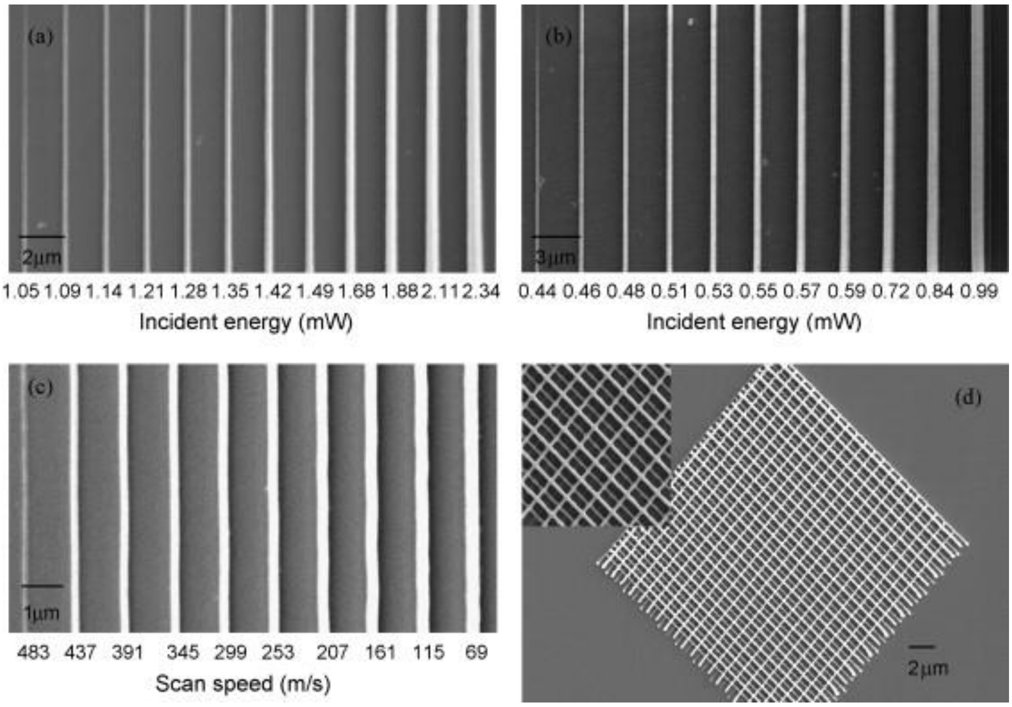


Figure 36. Examples of 2D and 3D patterns obtained by TPA photopolymerization experiments a) by using BZC36 and by modifying the intensity of the incident light b) by using the three-component BZC36/HABI/MMT and by modifying the intensity of the incident light c) by using the three-component BZC36/HABI/MMT at different scan speed d) by using BZC36 and 1.1mW power and 44 μm/s scan speed. Reproduced with permission of Ref. [393]

In 2010, influence of the substitution pattern was examined by comparing the photoinitiating abilities of 3-DAC and 4-DAC, the two dyes being isomers of positions (See Figure 37).[222]

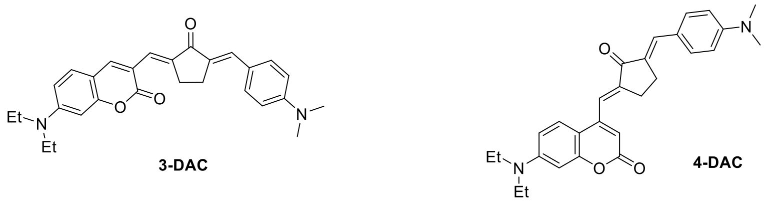


Figure 37. Chemical structure of 3-DAC and 4-DAC.

In this work, influence of the bridging position was found to have a dramatic effect on the π-conjugation as well as the photophysical and photochemical properties of the dyes. Notably, 3-DAC was found to exhibit a higher conjugation and a higher planarity than 4-DAC, resulting in turn in a larger TPA cross section (300 GM for 3-DAC vs. 107 GM for 4-DAC at 800 nm).

Possibility to design water-soluble asymmetric structures was also examined by Wu and coworkers.[396] In this aim, pyridinium and carboxylates groups were introduced as hydrophilic groups (See Figure 38). Even if two-photon polymerization experiments could be carried out with these two dyes, small two-photon absorption cross-sections were determined in the 720-880 nm range. Thus, a value of 113 GM was determined in chloroform for P1 whereas this value could not be determined for Y1, making these water-soluble dyes less interesting candidates for photopolymerization than their symmetric analogues (two-photon absorption cross-sections ranging between 231 and 808 GM for T1, BSEA and T3).

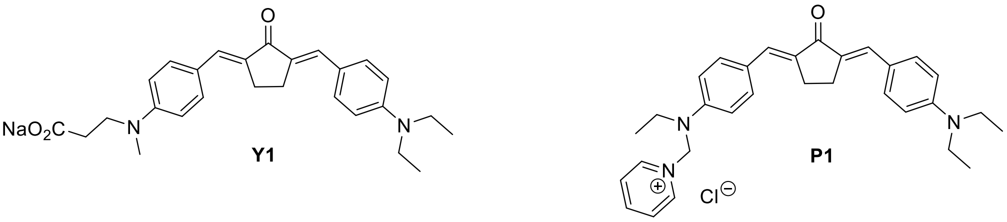
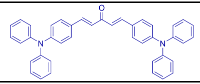
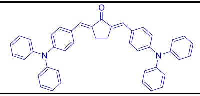
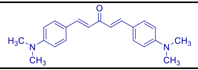
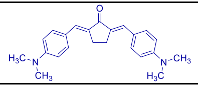
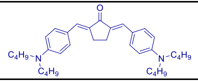
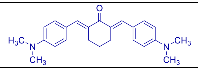
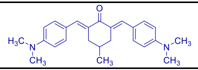
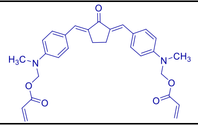
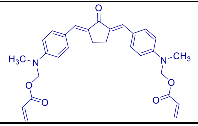
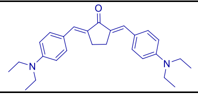
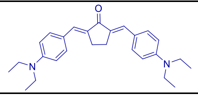
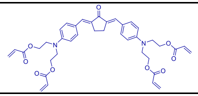
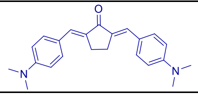
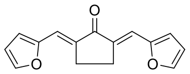
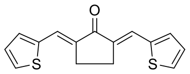
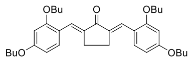
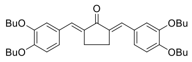
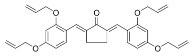
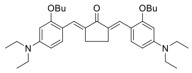
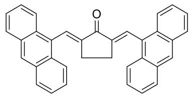
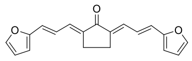
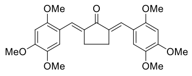
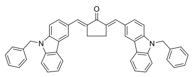
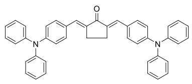
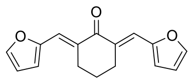
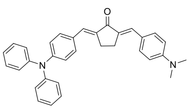
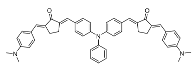
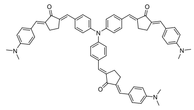
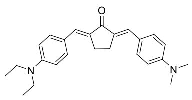
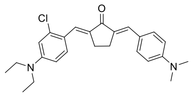
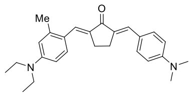
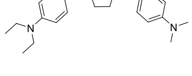


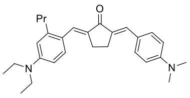
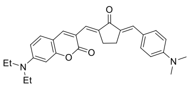
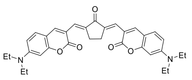
Figure 38. Different asymmetrically substituted water-soluble benzylidene cyclopentanones.

A summary of the optical properties as well as the monomer conversions obtained with the different benzylidene cyclopentanones is provided in the Table 5.

Dye	Chemical structure	Maximum absorption wavelength (nm)	Photoinitiating systems	Monomers	Light source	Monomer conversion	Ref.
2.1. chalcones							
BDPO		433	BDPO/NIOTf	PBOCS	780 nm	-	[310]
BDPA		459	BDPA/NIOTf	PBOCS	780 nm	-	[310]
BZC1		441	BZC1	TTA/ETA	780 nm	-	[305]
BZC2		466	BZC2	TTA/ETA	780 nm	-	[305]
BZC3		481	BZC3	TTA/ETA	780 nm	-	[305]
BZC4		432	BZC4	TTA/ETA	780 nm	-	[305]
BZC5		432	BZC5	TTA/ETA	780 nm	-	[305]

PBDA		473	PBDA	ETPTA	473 nm	57%	[336]
PBDA		473	PBDA	PEGDA	473 nm	68%	[336]
BDEA		487	BDEA	ETPTA	473 nm	43%	[336]
BDEA		487	BDEA	PEGDA	473 nm	46%	[336]
4Met-BAC		475	4Met-BAC	PETA	380 nm	21%	[354]
BZC2		475	BZC2	PETA	380 nm	10%	[354]
BZC16		396	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	76%	[176]
BZC17		392	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	93%	[176]
BZC18		400 274	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	96%	[176]
BZC19		399	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	80%	[176]
BZC20		460 274	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	73%	[176]
BZC21		397	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	83%	[176]
BZC22		485 278	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	75%	[176]
BZC23		418 268	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	92%	[176]
BZC24		428 283	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	90%	[176]
BZC25		427 280	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	75%	[176]
BZC26		421 236	dye/Iod/amine (0.1/1.5/1.5 wt%)	PEGDA	405	76%	[176]

BFC		400	2 wt% BFC/TEOA CTC	AM	405 nm	60%	[384]
BZC27		470	dye/Iod	2-phenoxy-ethyl acrylate/penta erythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w)	400-500 nm	62	[356]
BZC28		490	dye/Iod	2-phenoxy-ethyl acrylate/penta erythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w)	400-500 nm	70	[356]
BZC29		492	dye/Iod	2-phenoxy-ethyl acrylate/penta erythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w)	400-500 nm	70	[356]
BZC30		475	dye/HABI	2-phenoxy-ethyl acrylate/penta erythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w)	470 nm	55%	[390]
BZC31		470	dye/HABI	2-phenoxy-ethyl acrylate/penta erythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w)	470 nm	38%	[390]
BZC32		477	dye/HABI	2-phenoxy-ethyl acrylate/penta erythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w)	470 nm	65%	[390]
BZC33		475	dye/HABI	2-phenoxy-ethyl acrylate/penta erythritol triacrylate/	470 nm	60%	[390]

				epoxy acrylate (1/3/5 w/w/w)			
BZC34		475	dye/HABI	2-phenoxy-ethyl acrylate/penta erythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w)	470 nm	60%	[390]
BZC35		500	dye/Iod	2-phenoxy-ethyl acrylate/penta erythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w)	400-500 nm	65%	[393]
BZC36		521	dye/Iod	2-phenoxy-ethyl acrylate/penta erythritol triacrylate/ epoxy acrylate (1/3/5 w/w/w)	400-500 nm	65%	[393]

Conclusion

Benzylidene cyclopentanones have been extensively studied as one and two-photon photoinitiators. Even if numerous works were historically devoted to two-photon polymerization processes, recent works have clearly demonstrated their potential use as one-photon initiators. A great deal of efforts has notably been devoted to develop water-soluble dyes, enabling to elaborate greener polymerization processes. Superiority of benzylidene cyclopentanones over the other benzylidene ketone has been clearly evidenced, especially for tow-photon polymerization. Indeed, due to the rigidity provided by the central five-membered ring cycle, a dramatic enhancement of the two-photon absorption cross-section as well as presence of a wide fabrication window could be demonstrated. Among benzylidene cyclopentanones, BZC2 is undoubtedly the most widely studied structure since 1991. This is directly related to the fact that this dye can be prepared with cyclopentanone and 4-dimethylaminobenzaldehyde that are extremely cheap reagents. Besides, there are still rooms for improvements. Notably, at present, no type I photoinitiators have been designed with benzylidene cyclopentanones such as oxime esters[102,107,230,232,235,236,397–401] or glyoxylates for one photon polymerization.[402–405] Besides, it could greatly help to simplify the composition of the photocurable resins. Indeed, benzylidene cyclopentanones are efficient Type II photoinitiators but require the use of an additive. This issue could be addressed by developing monomolecular photoinitiators. Development of new benzylidene cyclopentanones based on glyoxylates or oximes esters is especially of crucial importance as it could be used in resins for 3D printing which is an additive manufacturing technique always in active development due to the growing market for this technology that is driving numerous innovations.

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Conflicts of Interest

The authors declare no conflict of interest.

References

[1] L. Pierau, C. Elian, J. Akimoto, Y. Ito, S. Caillol, D.-L. Versace, Bio-sourced monomers and cationic photopolymerization–The green combination towards eco-friendly and non-toxic materials, Prog. Polym. Sci. 127 (2022) 101517. https://doi.org/10.1016/j.progpolymsci.2022.101517.

[2] M.A. Tehfe, F. Louradour, J. Lalevée, J.-P. Fouassier, Photopolymerization Reactions: On the Way to a Green and Sustainable Chemistry, Appl. Sci. 3 (2013) 490–514. https://doi.org/10.3390/app3020490.

[3] R. Bongiovanni, S.D. Vacche, A. Vitale, Photoinduced Processes as a Way to Sustainable Polymers and Innovation in Polymeric Materials, Polymers. 13 (2021). https://doi.org/10.3390/polym13142293.

[4] V.S.D. Voet, J. Guit, K. Loos, Sustainable Photopolymers in 3D Printing: A Review on Biobased, Biodegradable, and Recyclable Alternatives, Macromol. Rapid Commun. 42 (2021) 2000475. https://doi.org/10.1002/marc.202000475.

[5] M.L. Allegrezza, Z.M. DeMartini, A.J. Kloster, Z.A. Digby, D. Konkolewicz, Visible and sunlight driven RAFT photopolymerization accelerated by amines: kinetics and mechanism, Polym. Chem. 7 (2016) 6626–6636. https://doi.org/10.1039/C6PY01433J.

[6] K. Sun, H. Chen, Y. Zhang, F. Morlet-Savary, B. Graff, P. Xiao, F. Dumur, J. Lalevée, High-performance sunlight induced polymerization using novel push-pull dyes with high light absorption properties, Eur. Polym. J. 151 (2021) 110410. https://doi.org/10.1016/j.eurpolymj.2021.110410.

[7] K. Sun, C. Pigot, Y. Zhang, T. Borjigin, F. Morlet-Savary, B. Graff, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, Sunlight Induced Polymerization Photoinitiated by Novel Push–Pull Dyes: Indane-1,3-Dione, 1H-Cyclopenta[b]Naphthalene-1,3(2H)-Dione and 4-Dimethoxyphenyl-1-Allylidene Derivatives, Macromol. Chem. Phys. 223 (2022) 2100439. https://doi.org/10.1002/macp.202100439.

[8] M. Ciftci, M.A. Tasdelen, Y. Yagci, Sunlight induced atom transfer radical polymerization by using dimanganese decacarbonyl, Polym. Chem. 5 (2014) 600–606. https://doi.org/10.1039/C3PY01009K.

[9] C. Decker, T. Bendaikha, Interpenetrating polymer networks. II. Sunlight-induced polymerization of multifunctional acrylates, J. Appl. Polym. Sci. 70 (1998) 2269–2282. https://doi.org/10.1002/(SICI)1097-4628(19981212)70:11<2269::AID-APP21>3.0.CO;2-D.

[10] M.-A. Tehfe, J. Lalevée, D. Gigmes, J.P. Fouassier, Green Chemistry: Sunlight-Induced Cationic Polymerization of Renewable Epoxy Monomers Under Air, Macromolecules. 43 (2010) 1364–1370. https://doi.org/10.1021/ma9025702.

[11] J. Wang, M. Rivero, A. Muñoz Bonilla, J. Sanchez-Marcos, W. Xue, G. Chen, W. Zhang, X. Zhu, Natural RAFT Polymerization: Recyclable-Catalyst-Aided, Opened-to-Air, and Sunlight-Photolyzed RAFT Polymerizations, ACS Macro Lett. 5 (2016) 1278–1282. https://doi.org/10.1021/acsmacrolett.6b00818.

[12] J. Yu, Y. Gao, S. Jiang, F. Sun, Naphthalimide Aryl Sulfide Derivative Norrish Type I Photoinitiators with Excellent Stability to Sunlight under Near-UV LED, Macromolecules. 52 (2019) 1707–1717. https://doi.org/10.1021/acs.macromol.8b02309.

[13] J. Shao, Y. Huang, Q. Fan, Visible light initiating systems for photopolymerization: status, development and challenges, Polym. Chem. 5 (2014) 4195–4210. https://doi.org/10.1039/C4PY00072B.

[14] B.K. Armstrong, A. Kricker, The epidemiology of UV induced skin cancer, Consequences Expo. Sunlightelements Assess Prot. 63 (2001) 8–18. https://doi.org/10.1016/S1011-1344(01)00198-1.

[15] F.R. de Gruijl, Skin cancer and solar UV radiation, Eur. J. Cancer. 35 (1999) 2003–2009. https://doi.org/10.1016/S0959-8049(99)00283-X.

[16] D.L. Narayanan, R.N. Saladi, J.L. Fox, Review: Ultraviolet radiation and skin cancer, Int. J. Dermatol. 49 (2010) 978–986. https://doi.org/10.1111/j.1365-4632.2010.04474.x.

[17] A.H. Bonardi, F. Dumur, T.M. Grant, G. Noirbent, D. Gigmes, B.H. Lessard, J.-P. Fouassier, J. Lalevée, High Performance Near-Infrared (NIR) Photoinitiating Systems Operating under Low Light Intensity and in the Presence of Oxygen, Macromolecules. 51 (2018) 1314–1324. https://doi.org/10.1021/acs.macromol.8b00051.

[18] P. Garra, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Photopolymerization processes of thick films and in shadow areas: a review for the access to composites, Polym. Chem. 8 (2017) 7088–7101. https://doi.org/10.1039/C7PY01778B.

[19] J. Lalevée, H. Mokbel, J.-P. Fouassier, Recent Developments of Versatile Photoinitiating Systems for Cationic Ring Opening Polymerization Operating at Any Wavelengths and under Low Light Intensity Sources, Molecules. 20 (2015) 7201–7221. https://doi.org/10.3390/molecules20047201.

[20] P. Xiao, J. Zhang, F. Dumur, M.A. Tehfe, F. Morlet-Savary, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Visible light sensitive photoinitiating systems: Recent progress in cationic and radical photopolymerization reactions under soft conditions, Prog. Polym. Sci. 41 (2015) 32–66. https://doi.org/10.1016/j.progpolymsci.2014.09.001.

[21] K. Sun, P. Xiao, F. Dumur, J. Lalevée, Organic dye-based photoinitiating systems for visible-light-induced photopolymerization, J. Polym. Sci. 59 (2021) 1338–1389. https://doi.org/10.1002/pol.20210225.

[22] J. Lalevée, S. Telitel, P. Xiao, M. Lepeltier, F. Dumur, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, Metal and metal-free photocatalysts: mechanistic approach and application as photoinitiators of photopolymerization, Beilstein J. Org. Chem. 10 (2014) 863–876. https://doi.org/10.3762/bjoc.10.83.

[23] P. Xiao, F. Dumur, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Cationic and Thiol–Ene Photopolymerization upon Red Lights Using Anthraquinone Derivatives as Photoinitiators, Macromolecules. 46 (2013) 6744–6750. https://doi.org/10.1021/ma401513b.

[24] M.-A. Tehfe, D. Gigmes, F. Dumur, D. Bertin, F. Morlet-Savary, B. Graff, J. Lalevée, J.-P. Fouassier, Cationic photosensitive formulations based on silyl radical chemistry for green and red diode laser exposure, Polym. Chem. 3 (2012) 1899–1902. https://doi.org/10.1039/C1PY00460C.

[25] P. Garra, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Redox two-component initiated free radical and cationic polymerizations: Concepts, reactions and applications, Prog. Polym. Sci. 94 (2019) 33–56. https://doi.org/10.1016/j.progpolymsci.2019.04.003.

[26] Y. Zhang, Y. Xu, A. Simon-Masseron, J. Lalevée, Radical photoinitiation with LEDs and applications in the 3D printing of composites, Chem. Soc. Rev. 50 (2021) 3824–3841. https://doi.org/10.1039/D0CS01411G.

[27] F. Dumur, Recent Advances on Visible Light Metal-Based Photocatalysts for Polymerization under Low Light Intensity, Catalysts. 9 (2019) 736. https://doi.org/10.3390/catal9090736.

[28] C. Pigot, G. Noirbent, D. Brunel, F. Dumur, Recent advances on push–pull organic dyes as visible light photoinitiators of polymerization, Eur. Polym. J. 133 (2020) 109797. https://doi.org/10.1016/j.eurpolymj.2020.109797.

[29] W. Tomal, J. Ortyl, Water-Soluble Photoinitiators in Biomedical Applications, Polymers. 12 (2020) 1073. https://doi.org/10.3390/polym12051073.

[30] N. Corrigan, J. Yeow, P. Judzewitsch, J. Xu, C. Boyer, Seeing the Light: Advancing Materials Chemistry through Photopolymerization, Angew. Chem. Int. Ed. 58 (2019) 5170–5189. https://doi.org/10.1002/anie.201805473.

[31] A. Banerji, K. Jin, K. Liu, M.K. Mahanthappa, C.J. Ellison, Cross-Linked Nonwoven Fibers by Room-Temperature Cure Blowing and in Situ Photopolymerization, Macromolecules. 52 (2019) 6662–6672. https://doi.org/10.1021/acs.macromol.9b01002.

[32] G. Yilmaz, Y. Yagci, Light-induced step-growth polymerization, Prog. Polym. Sci. 100 (2020) 101178. https://doi.org/10.1016/j.progpolymsci.2019.101178.

[33] M. Layani, X. Wang, S. Magdassi, Novel Materials for 3D Printing by Photopolymerization, Adv. Mater. 30 (2018) 1706344. https://doi.org/10.1002/adma.201706344.

[34] C. Dietlin, S. Schweizer, P. Xiao, J. Zhang, F. Morlet-Savary, B. Graff, J.-P. Fouassier, J. Lalevée, Photopolymerization upon LEDs: new photoinitiating systems and strategies, Polym. Chem. 6 (2015) 3895–3912. https://doi.org/10.1039/C5PY00258C.

[35] S. Shanmugam, J. Xu, C. Boyer, Photocontrolled Living Polymerization Systems with Reversible Deactivations through Electron and Energy Transfer, Macromol. Rapid Commun. 38 (2017) 1700143. https://doi.org/10.1002/marc.201700143.

[36] F. Jasinski, P.B. Zetterlund, A.M. Braun, A. Chemtob, Photopolymerization in dispersed systems, Prog. Polym. Sci. 84 (2018) 47–88. https://doi.org/10.1016/j.progpolymsci.2018.06.006.

[37] C. Noè, M. Hakkarainen, M. Sangermano, Cationic UV-Curing of Epoxidized Biobased Resins, Polymers. 13 (2021) 89. https://doi.org/10.3390/polym13010089.

[38] Y. Yuan, C. Li, R. Zhang, R. Liu, J. Liu, Low volume shrinkage photopolymerization system using hydrogen-bond-based monomers, Prog. Org. Coat. 137 (2019) 105308. https://doi.org/10.1016/j.porgcoat.2019.105308.

[39] I.V. Khudyakov, J.C. Legg, M.B. Purvis, B.J. Overton, Kinetics of Photopolymerization of Acrylates with Functionality of 1−6, Ind. Eng. Chem. Res. 38 (1999) 3353–3359. https://doi.org/10.1021/ie990306i.

[40] S.H. Dickens, J.W. Stansbury, K.M. Choi, C.J.E. Floyd, Photopolymerization Kinetics of Methacrylate Dental Resins, Macromolecules. 36 (2003) 6043–6053. https://doi.org/10.1021/ma021675k.

[41] A. Maffezzoli, A.D. Pietra, S. Rengo, L. Nicolais, G. Valletta, Photopolymerization of dental composite matrices, Biomaterials. 15 (1994) 1221–1228. https://doi.org/10.1016/0142-9612(94)90273-9.

[42] T. Dikova, J. Maximov, V. Todorov, G. Georgiev, V. Panov, Optimization of Photopolymerization Process of Dental Composites, Processes. 9 (2021) 779. https://doi.org/10.3390/pr9050779.

[43] A. Andreu, P.-C. Su, J.-H. Kim, C.S. Ng, S. Kim, I. Kim, J. Lee, J. Noh, A.S. Subramanian, Y.-J. Yoon, 4D printing materials for vat photopolymerization, Addit. Manuf. 44 (2021) 102024. https://doi.org/10.1016/j.addma.2021.102024.

[44] H. Chen, G. Noirbent, Y. Zhang, K. Sun, S. Liu, D. Brunel, D. Gigmes, B. Graff, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, Photopolymerization and 3D/4D applications using newly developed dyes: Search around the natural chalcone scaffold in photoinitiating systems, Dyes Pigments. 188 (2021) 109213. https://doi.org/10.1016/j.dyepig.2021.109213.

[45] A. Bagheri, J. Jin, Photopolymerization in 3D Printing, ACS Appl. Polym. Mater. 1 (2019) 593–611. https://doi.org/10.1021/acsapm.8b00165.

[46] A. Al Mousawi, P. Garra, X. Sallenave, F. Dumur, J. Toufaily, T. Hamieh, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, π-Conjugated Dithienophosphole Derivatives as High Performance Photoinitiators for 3D Printing Resins, Macromolecules. 51 (2018) 1811–1821. https://doi.org/10.1021/acs.macromol.8b00044.

[47] F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Organic Electronics: An El Dorado in the Quest of New Photocatalysts for Polymerization Reactions, Acc. Chem. Res. 49 (2016) 1980–1989. https://doi.org/10.1021/acs.accounts.6b00227.

[48] M.-A. Tehfe, F. Dumur, S. Telitel, D. Gigmes, E. Contal, D. Bertin, F. Morlet-Savary, B. Graff, J.-P. Fouassier, J. Lalevée, Zinc-based metal complexes as new photocatalysts in polymerization initiating systems, Eur. Polym. J. 49 (2013) 1040–1049. https://doi.org/10.1016/j.eurpolymj.2013.01.023.

[49] J. Zhang, N. Zivic, F. Dumur, C. Guo, Y. Li, P. Xiao, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Panchromatic photoinitiators for radical, cationic and thiol-ene polymerization reactions: A search in the diketopyrrolopyrrole or indigo dye series, Mater. Today Commun. 4 (2015) 101–108. https://doi.org/10.1016/j.mtcomm.2015.06.007.

[50] P. Xiao, W. Hong, Y. Li, F. Dumur, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Diketopyrrolopyrrole dyes: Structure/reactivity/efficiency relationship in photoinitiating systems upon visible lights, Polymer. 55 (2014) 746–751. https://doi.org/10.1016/j.polymer.2014.01.003.

[51] P. Xiao, W. Hong, Y. Li, F. Dumur, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Green light sensitive diketopyrrolopyrrole derivatives used in versatile photoinitiating

systems for photopolymerizations, Polym. Chem. 5 (2014) 2293–2300. https://doi.org/10.1039/C3PY01599H.

[52] J. Lalevée, M. Peter, F. Dumur, D. Gigmes, N. Blanchard, M.-A. Tehfe, F. Morlet-Savary, J.P. Fouassier, Subtle Ligand Effects in Oxidative Photocatalysis with Iridium Complexes: Application to Photopolymerization, Chem. – Eur. J. 17 (2011) 15027–15031. https://doi.org/10.1002/chem.201101445.

[53] J. Lalevée, M.-A. Tehfe, F. Dumur, D. Gigmes, N. Blanchard, F. Morlet-Savary, J.P. Fouassier, Iridium Photocatalysts in Free Radical Photopolymerization under Visible Lights, ACS Macro Lett. 1 (2012) 286–290. https://doi.org/10.1021/mz2001753.

[54] J. Lalevée, F. Dumur, C.R. Mayer, D. Gigmes, G. Nasr, M.-A. Tehfe, S. Telitel, F. Morlet-Savary, B. Graff, J.P. Fouassier, Photopolymerization of N-Vinylcarbazole Using Visible-Light Harvesting Iridium Complexes as Photoinitiators, Macromolecules. 45 (2012) 4134–4141. https://doi.org/10.1021/ma3005229.

[55] M.-A. Tehfe, M. Lepeltier, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Structural Effects in the Iridium Complex Series: Photoredox Catalysis and Photoinitiation of Polymerization Reactions under Visible Lights, Macromol. Chem. Phys. 218 (2017) 1700192. https://doi.org/10.1002/macp.201700192.

[56] S. Telitel, F. Dumur, S. Telitel, O. Soppera, M. Lepeltier, Y. Guillaneuf, J. Poly, F. Morlet-Savary, P. Fioux, J.-P. Fouassier, D. Gigmes, J. Lalevée, Photoredox catalysis using a new iridium complex as an efficient toolbox for radical, cationic and controlled polymerizations under soft blue to green lights, Polym. Chem. 6 (2014) 613–624. https://doi.org/10.1039/C4PY01358A.

[57] S. Telitel, F. Dumur, M. Lepeltier, D. Gigmes, J.-P. Fouassier, J. Lalevée, Photoredox process induced polymerization reactions: Iridium complexes for panchromatic photoinitiating systems, Comptes Rendus Chim. 19 (2016) 71–78. https://doi.org/10.1016/j.crci.2015.06.016.

[58] F. Dumur, D. Bertin, D. Gigmes, Iridium (III) complexes as promising emitters for solid–state Light–Emitting Electrochemical Cells (LECs), Int. J. Nanotechnol. 9 (2012) 377–395. https://doi.org/10.1504/IJNT.2012.045343.

[59] F. Dumur, G. Nasr, G. Wantz, C.R. Mayer, E. Dumas, A. Guerlin, F. Miomandre, G. Clavier, D. Bertin, D. Gigmes, Cationic iridium complex for the design of soft salt-based phosphorescent OLEDs and color-tunable light-emitting electrochemical cells, Org. Electron. 12 (2011) 1683–1694. https://doi.org/10.1016/j.orgel.2011.06.014.

[60] C. Brahmi, M. Benltifa, C. Vaulot, L. Michelin, F. Dumur, F. Millange, M. Frigoli, A. Airoudj, F. Morlet-Savary, L. Bousselmi, J. Lalevée, New hybrid MOF/polymer composites for the photodegradation of organic dyes, Eur. Polym. J. 154 (2021) 110560. https://doi.org/10.1016/j.eurpolymj.2021.110560.

[61] J. Zhang, F. Dumur, P. Horcajada, C. Livage, P. Xiao, J.P. Fouassier, D. Gigmes, J. Lalevée, Iron-Based Metal-Organic Frameworks (MOF) as Photocatalysts for Radical and Cationic Polymerizations under Near UV and Visible LEDs (385–405 nm), Macromol. Chem. Phys. 217 (2016) 2534–2540. https://doi.org/10.1002/macp.201600352.

[62] C. Brahmi, M. Benltifa, C. Vaulot, L. Michelin, F. Dumur, E. Gkaniatsou, C. Sicard, A. Airoudj, F. Morlet-Savary, L. Bousselmi, J. Lalevée, New Hybrid Fe-based MOFs/Polymer Composites for the Photodegradation of Organic Dyes, ChemistrySelect. 6 (2021) 8120–8132. https://doi.org/10.1002/slct.202102194.

[63] A.A. Mousawi, F. Dumur, P. Garra, J. Toufaily, T. Hamieh, F. Goubard, T.-T. Bui, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Azahelicenes as visible light photoinitiators

for cationic and radical polymerization: Preparation of photoluminescent polymers and use in high performance LED projector 3D printing resins, J. Polym. Sci. Part Polym. Chem. 55 (2017) 1189–1199. https://doi.org/10.1002/pola.28476.

[64] A. Al Mousawi, M. Schmitt, F. Dumur, J. Ouyang, L. Favereau, V. Dorcet, N. Vanthuyne, P. Garra, J. Toufaily, T. Hamieh, B. Graff, J.P. Fouassier, D. Gigmes, J. Crassous, J. Lalevée, Visible Light Chiral Photoinitiator for Radical Polymerization and Synthesis of Polymeric Films with Strong Chiroptical Activity, Macromolecules. 51 (2018) 5628–5637. https://doi.org/10.1021/acs.macromol.8b01085.

[65] B. Bao, J. You, D. Li, H. Zhan, L. Zhang, M. Li, T. Wang, Double benzylidene ketones as photoinitiators for visible light photopolymerization, J. Photochem. Photobiol. Chem. 429 (2022) 113938. https://doi.org/10.1016/j.jphotochem.2022.113938.

[66] H. Fu, Y. Qiu, J. You, T. Hao, B. Fan, J. Nie, T. Wang, Photopolymerization of acrylate resin and ceramic suspensions with benzylidene ketones under blue/green LED, Polymer. 184 (2019) 121841. https://doi.org/10.1016/j.polymer.2019.121841.

[67] F. Dumur, Recent advances on visible light Phenothiazine-based photoinitiators of polymerization, Eur. Polym. J. 165 (2022) 110999. https://doi.org/10.1016/j.eurpolymj.2022.110999.

[68] L. Deng, L. Tang, J. Qu, Novel chalcone-based phenothiazine derivative photoinitiators for visible light induced photopolymerization with photobleaching and good biocompatibility, Prog. Org. Coat. 167 (2022) 106859. https://doi.org/10.1016/j.porgcoat.2022.106859.

[69] M. Rahal, M. Abdallah, T.-T. Bui, F. Goubard, B. Graff, F. Dumur, J. Toufaily, T. Hamieh, J. Lalevée, Design of new phenothiazine derivatives as visible light photoinitiators, Polym. Chem. 11 (2020) 3349–3359. https://doi.org/10.1039/D0PY00497A.

[70] S. Li, J. Hu, S. Zhang, C. Feng, L. Zhang, C. Wang, Z. He, L. Zhang, Novel A-π-D-π-A structure two-photon polymerization initiators based on phenothiazine and carbazole derivatives, Chem. Pap. 75 (2021) 5249–5256. https://doi.org/10.1007/s11696-021-01713-9.

[71] D.F. Grishin, O.S. Lizyakina, L.B. Vaganova, A.A. Kaltenberg, I.D. Grishin, Radical polymerization of methyl methacrylate in the presence of methylene blue and organobromides under visible light irradiation, Iran. Polym. J. 30 (2021) 1117–1126. https://doi.org/10.1007/s13726-021-00951-8.

[72] D. Xu, X. Zou, Y. Zhu, Z. Yu, M. Jin, R. Liu, Phenothiazine-based charge-transfer complexes as visible-light photoinitiating systems for acrylate and thiol-ene photopolymerization, Prog. Org. Coat. 166 (2022) 106772. https://doi.org/10.1016/j.porgcoat.2022.106772.

[73] Y. Zhu, D. Xu, Y. Zhang, Y. Zhou, Y. Yagci, R. Liu, Phenacyl Phenothiazinium Salt as a New Broad-Wavelength-Absorbing Photoinitiator for Cationic and Free Radical Polymerizations, Angew. Chem. Int. Ed. 60 (2021) 16917–16921. https://doi.org/10.1002/anie.202104531.

[74] P. Chao, R. Gu, X. Ma, T. Wang, Y. Zhao, Thiophene-substituted phenothiazine-based photosensitisers for radical and cationic photopolymerization reactions under visible laser beams (405 and 455 nm), Polym. Chem. 7 (2016) 5147–5156. https://doi.org/10.1039/C6PY01095D.

[75] T.F. Zhou, X.Y. Ma, W.X. Han, X.P. Guo, R.Q. Gu, L.J. Yu, J. Li, Y.M. Zhao, T. Wang, D–D–A dyes with phenothiazine–carbazole/triphenylamine as double donors in photopolymerization under 455 nm and 532 nm laser beams11Electronic

supplementary information (ESI) available: Detailed synthesis of all dyes and associated spectra. See DOI: 10.1039/c6py00918b, Polym. Chem. 7 (2016) 5039–5049. https://doi.org/10.1039/c6py00918b.

[76] M. Wang, X. Ma, J. Yu, X. Jia, D. Han, T. Zhou, J. Yang, J. Nie, T. Wang, Aromatic amine–sulfone/sulfoxide conjugated D–π-A–π-D-type dyes in photopolymerization under 405 nm and 455 nm laser beams, Polym. Chem. 6 (2015) 4424–4435. https://doi.org/10.1039/C5PY00502G.

[77] F. Hao, Z. Liu, M. Zhang, J. Liu, S. Zhang, J. Wu, H. Zhou, Y. Tian, Four new two-photon polymerization initiators with varying donor and conjugated bridge: Synthesis and two-photon activity, Spectrochim. Acta. A. Mol. Biomol. Spectrosc. 118 (2014) 538–542. https://doi.org/10.1016/j.saa.2013.09.051.

[78] E.A. Kamoun, A. Winkel, M. Eisenburger, H. Menzel, Carboxylated camphorquinone as visible-light photoinitiator for biomedical application: Synthesis, characterization, and application, Arab. J. Chem. 9 (2016) 745–754. https://doi.org/10.1016/j.arabjc.2014.03.008.

[79] A. Santini, I.T. Gallegos, C.M. Felix, Photoinitiators in Dentistry: A Review, Prim. Dent. J. 2 (2013) 30–33. https://doi.org/10.1308/205016814809859563.

[80] J. Zhao, J. Lalevée, H. Lu, R. MacQueen, S.H. Kable, T.W. Schmidt, M.H. Stenzel, P. Xiao, A new role of curcumin: as a multicolor photoinitiator for polymer fabrication under household UV to red LED bulbs, Polym. Chem. 6 (2015) 5053–5061. https://doi.org/10.1039/C5PY00661A.

[81] J.V. Crivello, U. Bulut, Curcumin: A naturally occurring long-wavelength photosensitizer for diaryliodonium salts, J. Polym. Sci. Part Polym. Chem. 43 (2005) 5217–5231. https://doi.org/10.1002/pola.21017.

[82] W. Han, H. Fu, T. Xue, T. Liu, Y. Wang, T. Wang, Facilely prepared blue-green light sensitive curcuminoids with excellent bleaching properties as high performance photosensitizers in cationic and free radical photopolymerization, Polym. Chem. 9 (2018) 1787–1798. https://doi.org/10.1039/C8PY00166A.

[83] A. Mishra, S. Daswal, Curcumin, A Novel Natural Photoinitiator for the Copolymerization of Styrene and Methylmethacrylate, J. Macromol. Sci. Part A. 42 (2005) 1667–1678. https://doi.org/10.1080/10601320500246974.

[84] P. Garra, D. Brunel, G. Noirbent, B. Graff, F. Morlet-Savary, C. Dietlin, V.F. Sidorkin, F. Dumur, D. Duché, D. Gigmes, J.-P. Fouassier, J. Lalevée, Ferrocene-based (photo)redox polymerization under long wavelengths, Polym. Chem. 10 (2019) 1431–1441. https://doi.org/10.1039/C9PY00059C.

[85] M.-A. Tehfe, A. Zein-Fakih, J. Lalevée, F. Dumur, D. Gigmes, B. Graff, F. Morlet-Savary, T. Hamieh, J.-P. Fouassier, New pyridinium salts as versatile compounds for dye sensitized photopolymerization, Eur. Polym. J. 49 (2013) 567–574. https://doi.org/10.1016/j.eurpolymj.2012.10.010.

[86] P. Xiao, M. Frigoli, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Julolidine or Fluorenone Based Push–Pull Dyes for Polymerization upon Soft Polychromatic Visible Light or Green Light., Macromolecules. 47 (2014) 106–112. https://doi.org/10.1021/ma402196p.

[87] H. Mokbel, F. Dumur, B. Graff, C.R. Mayer, D. Gigmes, J. Toufaily, T. Hamieh, J.-P. Fouassier, J. Lalevée, Michler's Ketone as an Interesting Scaffold for the Design of High-Performance Dyes in Photoinitiating Systems Upon Visible Light, Macromol. Chem. Phys. 215 (2014) 783–790. https://doi.org/10.1002/macp.201300779.

[88] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gigmes, J. Lalevée, New Push–Pull Dyes Derived from Michler's Ketone For Polymerization Reactions Upon Visible Lights., Macromolecules. 46 (2013) 3761–3770. https://doi.org/10.1021/ma400766z.

[89] H. Mokbel, F. Dumur, C.R. Mayer, F. Morlet-Savary, B. Graff, D. Gigmes, J. Toufaily, T. Hamieh, J.-P. Fouassier, J. Lalevée, End capped polyenic structures as visible light sensitive photoinitiators for polymerization of vinylethers, Dyes Pigments. 105 (2014) 121–129. https://doi.org/10.1016/j.dyepig.2014.02.002.

[90] S. Telitel, F. Dumur, T. Kavalli, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, The 1,3-bis(dicyanomethylidene)indane skeleton as a (photo) initiator in thermal ring opening polymerization at RT and radical or cationic photopolymerization, RSC Adv. 4 (2014) 15930–15936. https://doi.org/10.1039/C3RA42819B.

[91] P. Xiao, F. Dumur, B. Graff, F. Morlet-Savary, L. Vidal, D. Gigmes, J.P. Fouassier, J. Lalevée, Structural Effects in the Indanedione Skeleton for the Design of Low Intensity 300–500 nm Light Sensitive Initiators., Macromolecules. 47 (2014) 26–34. https://doi.org/10.1021/ma402149g.

[92] K. Sun, S. Liu, C. Pigot, D. Brunel, B. Graff, M. Nechab, D. Gigmes, F. Morlet-Savary, Y. Zhang, P. Xiao, F. Dumur, J. Lalevée, Novel Push–Pull Dyes Derived from 1H-cyclopenta[b]naphthalene-1,3(2H)-dione as Versatile Photoinitiators for Photopolymerization and Their Related Applications: 3D Printing and Fabrication of Photocomposites, Catalysts. 10 (2020) 1196. https://doi.org/10.3390/catal10101196.

[93] K. Sun, S. Liu, H. Chen, F. Morlet-Savary, B. Graff, C. Pigot, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, N-ethyl carbazole-1-allylidene-based push-pull dyes as efficient light harvesting photoinitiators for sunlight induced polymerization, Eur. Polym. J. 147 (2021) 110331. https://doi.org/10.1016/j.eurpolymj.2021.110331.

[94] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, Push–pull (thio)barbituric acid derivatives in dye photosensitized radical and cationic polymerization reactions under 457/473 nm laser beams or blue LEDs, Polym. Chem. 4 (2013) 3866–3875. https://doi.org/10.1039/C3PY00372H.

[95] H. Mokbel, F. Dumur, S. Telitel, L. Vidal, P. Xiao, D.-L. Versace, M.-A. Tehfe, F. Morlet-Savary, B. Graff, J.-P. Fouassier, D. Gigmes, J. Toufaily, T. Hamieh, J. Lalevée, Photoinitiating systems of polymerization and in situ incorporation of metal nanoparticles into polymer matrices upon exposure to visible light: push–pull malonate and malononitrile based dyes, Polym. Chem. 4 (2013) 5679–5687. https://doi.org/10.1039/C3PY00846K.

[96] S. Helmy, S. Oh, F.A. Leibfarth, C.J. Hawker, J. Read de Alaniz, Design and Synthesis of Donor–Acceptor Stenhouse Adducts: A Visible Light Photoswitch Derived from Furfural, J. Org. Chem. 79 (2014) 11316–11329. https://doi.org/10.1021/jo502206g.

[97] M. Abdallah, A. Hijazi, B. Graff, J.-P. Fouassier, G. Rodeghiero, A. Gualandi, F. Dumur, P.G. Cozzi, J. Lalevée, Coumarin derivatives as versatile photoinitiators for 3D printing, polymerization in water and photocomposite synthesis, Polym. Chem. 10 (2019) 872–884. https://doi.org/10.1039/C8PY01708E.

[98] M. Abdallah, F. Dumur, A. Hijazi, G. Rodeghiero, A. Gualandi, P.G. Cozzi, J. Lalevée, Keto-coumarin scaffold for photoinitiators for 3D printing and photocomposites, J. Polym. Sci. 58 (2020) 1115–1129. https://doi.org/10.1002/pol.20190290.

[99] M. Abdallah, A. Hijazi, F. Dumur, J. Lalevée, Coumarins as Powerful Photosensitizers for the Cationic Polymerization of Epoxy-Silicones under Near-UV and Visible Light and Applications for 3D Printing Technology, Molecules. 25 (2020) 2063. https://doi.org/10.3390/molecules25092063.

[100] M. Abdallah, A. Hijazi, P.G. Cozzi, A. Gualandi, F. Dumur, J. Lalevée, Boron Compounds as Additives for the Cationic Polymerization Using Coumarin Derivatives in Epoxy Silicones, Macromol. Chem. Phys. 222 (2021) 2000404. https://doi.org/10.1002/macp.202000404.

[101] Q. Chen, Q. Yang, P. Gao, B. Chi, J. Nie, Y. He, Photopolymerization of Coumarin-Containing Reversible Photoresponsive Materials Based on Wavelength Selectivity, Ind. Eng. Chem. Res. 58 (2019) 2970–2975. https://doi.org/10.1021/acs.iecr.8b05164.

[102] Z. Li, X. Zou, G. Zhu, X. Liu, R. Liu, Coumarin-Based Oxime Esters: Photobleachable and Versatile Unimolecular Initiators for Acrylate and Thiol-Based Click Photopolymerization under Visible Light-Emitting Diode Light Irradiation, ACS Appl. Mater. Interfaces. 10 (2018) 16113–16123. https://doi.org/10.1021/acsami.8b01767.

[103] M. Rahal, H. Mokbel, B. Graff, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, Mono vs. Difunctional Coumarin as Photoinitiators in Photocomposite Synthesis and 3D Printing, Catalysts. 10 (2020) 1202. https://doi.org/10.3390/catal10101202.

[104] M. Rajeshirke, M.C. Sreenath, S. Chitrambalam, I.H. Joe, N. Sekar, Enhancement of NLO Properties in OBO Fluorophores Derived from Carbazole–Coumarin Chalcones Containing Carboxylic Acid at the N-Alykl Terminal End, J. Phys. Chem. C. 122 (2018) 14313–14325. https://doi.org/10.1021/acs.jpcc.8b02937.

[105] M. Rahal, B. Graff, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, Design of keto-coumarin based photoinitiator for Free Radical Photopolymerization: Towards 3D printing and photocomposites applications, Eur. Polym. J. 154 (2021) 110559. https://doi.org/10.1016/j.eurpolymj.2021.110559.

[106] M. Rahal, B. Graff, J. Toufaily, T. Hamieh, G. Noirbent, D. Gigmes, F. Dumur, J. Lalevée, 3-Carboxylic Acid and Formyl-Derived Coumarins as Photoinitiators in Photo-Oxidation or Photo-Reduction Processes for Photopolymerization upon Visible Light: Photocomposite Synthesis and 3D Printing Applications, Molecules. 26 (2021). https://doi.org/10.3390/molecules26061753.

[107] F. Hammoud, N. Giacoletto, G. Noirbent, B. Graff, A. Hijazi, M. Nechab, D. Gigmes, F. Dumur, J. Lalevée, Substituent effects on the photoinitiation ability of coumarin-based oxime-ester photoinitiators for free radical photopolymerization, Mater. Chem. Front. 5 (2021) 8361–8370. https://doi.org/10.1039/D1QM01310F.

[108] F. Dumur, Recent advances on coumarin-based photoinitiators of polymerization, Eur. Polym. J. 163 (2022) 110962. https://doi.org/10.1016/j.eurpolymj.2021.110962.

[109] Z. Liu, F. Dumur, Recent advances on visible light Coumarin-based oxime esters as initiators of polymerization, Eur. Polym. J. 177 (2022) 111449. https://doi.org/10.1016/j.eurpolymj.2022.111449.

[110] P. Xiao, F. Dumur, M. Frigoli, B. Graff, F. Morlet-Savary, G. Wantz, H. Bock, J.P. Fouassier, D. Gigmes, J. Lalevée, Perylene derivatives as photoinitiators in blue light sensitive cationic or radical curable films and panchromatic thiol-ene polymerizable films, Eur. Polym. J. 53 (2014) 215–222. https://doi.org/10.1016/j.eurpolymj.2014.01.024.

[111] P. Xiao, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Red-Light-Induced Cationic Photopolymerization: Perylene Derivatives as Efficient Photoinitiators,

Macromol. Rapid Commun. 34 (2013) 1452–1458. https://doi.org/10.1002/marc.201300383.

[112] F. Dumur, Recent advances on perylene-based photoinitiators of polymerization, Eur. Polym. J. 159 (2021) 110734. https://doi.org/10.1016/j.eurpolymj.2021.110734.

[113] M.-A. Tehfe, F. Dumur, B. Graff, D. Gigmes, J.-P. Fouassier, J. Lalevée, Green-Light-Induced Cationic Ring Opening Polymerization Reactions: Perylene-3,4:9,10-bis(Dicarboximide) as Efficient Photosensitizers, Macromol. Chem. Phys. 214 (2013) 1052–1060. https://doi.org/10.1002/macp.201200728.

[114] B. Corakci, S.O. Hacioglu, L. Toppare, U. Bulut, Long wavelength photosensitizers in photoinitiated cationic polymerization: The effect of quinoxaline derivatives on photopolymerization, Polymer. 54 (2013) 3182–3187. https://doi.org/10.1016/j.polymer.2013.04.008.

[115] P. Xiao, F. Dumur, D. Thirion, S. Fagour, A. Vacher, X. Sallenave, F. Morlet-Savary, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Multicolor Photoinitiators for Radical and Cationic Polymerization: Monofunctional vs Polyfunctional Thiophene Derivatives, Macromolecules. 46 (2013) 6786–6793. https://doi.org/10.1021/ma401389t.

[116] F. Dumur, C.R. Mayer, E. Dumas, F. Miomandre, M. Frigoli, F. Sécheresse, New Chelating Stilbazonium-Like Dyes from Michler's Ketone, Org. Lett. 10 (2008) 321–324. https://doi.org/10.1021/ol702793j.

[117] L. Cao, Y. Wang, Photocatalysis of viologens for photoinitiated polymerization using carboxylic acid as electron donors, J. Photochem. Photobiol. Chem. 333 (2017) 63–69. https://doi.org/10.1016/j.jphotochem.2016.10.019.

[118] W. Schnabel, Cationic photopolymerization with the aid of pyridinium-type salts, Macromol. Rapid Commun. 21 (2000) 628–642. https://doi.org/10.1002/1521-3927(20000601)21:10<628::AID-MARC628>3.0.CO;2-Q.

[119] P. Xiao, F. Dumur, J. Zhang, J.P. Fouassier, D. Gigmes, J. Lalevée, Copper Complexes in Radical Photoinitiating Systems: Applications to Free Radical and Cationic Polymerization upon Visible LEDs, Macromolecules. 47 (2014) 3837–3844. https://doi.org/10.1021/ma5006793.

[120] P. Xiao, F. Dumur, J. Zhang, D. Gigmes, J.P. Fouassier, J. Lalevée, Copper complexes: the effect of ligands on their photoinitiation efficiencies in radical polymerization reactions under visible light, Polym. Chem. 5 (2014) 6350–6357. https://doi.org/10.1039/C4PY00925H.

[121] P. Xiao, J. Zhang, D. Campolo, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, Copper and iron complexes as visible-light-sensitive photoinitiators of polymerization, J. Polym. Sci. Part Polym. Chem. 53 (2015) 2673–2684. https://doi.org/10.1002/pola.27762.

[122] P. Garra, M. Carré, F. Dumur, F. Morlet-Savary, C. Dietlin, D. Gigmes, J.-P. Fouassier, J. Lalevée, Copper-Based (Photo)redox Initiating Systems as Highly Efficient Systems for Interpenetrating Polymer Network Preparation, Macromolecules. 51 (2018) 679–688. https://doi.org/10.1021/acs.macromol.7b02491.

[123] P. Garra, F. Dumur, F. Morlet-Savary, C. Dietlin, D. Gigmes, J.P. Fouassier, J. Lalevée, Mechanosynthesis of a Copper complex for redox initiating systems with a unique near infrared light activation, J. Polym. Sci. Part Polym. Chem. 55 (2017) 3646–3655. https://doi.org/10.1002/pola.28750.

[124] P. Garra, F. Dumur, A.A. Mousawi, B. Graff, D. Gigmes, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, Mechanosynthesized copper(I) complex based initiating

systems for redox polymerization: towards upgraded oxidizing and reducing agents, Polym. Chem. 8 (2017) 5884–5896. https://doi.org/10.1039/C7PY01244F.

[125] H. Mokbel, D. Anderson, R. Plenderleith, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Copper photoredox catalyst "G1": a new high performance photoinitiator for near-UV and visible LEDs, Polym. Chem. 8 (2017) 5580–5592. https://doi.org/10.1039/C7PY01016H.

[126] H. Mokbel, D. Anderson, R. Plenderleith, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, Simultaneous initiation of radical and cationic polymerization reactions using the "G1" copper complex as photoredox catalyst: Applications of free radical/cationic hybrid photopolymerization in the composites and 3D printing fields, Prog. Org. Coat. 132 (2019) 50–61. https://doi.org/10.1016/j.porgcoat.2019.02.044.

[127] A.A. Mousawi, A. Kermagoret, D.-L. Versace, J. Toufaily, T. Hamieh, B. Graff, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, Copper photoredox catalysts for polymerization upon near UV or visible light: structure/reactivity/efficiency relationships and use in LED projector 3D printing resins, Polym. Chem. 8 (2017) 568–580. https://doi.org/10.1039/C6PY01958G.

[128] A. Mau, G. Noirbent, C. Dietlin, B. Graff, D. Gigmes, F. Dumur, J. Lalevée, Panchromatic Copper Complexes for Visible Light Photopolymerization, Photochem. 1 (2021). https://doi.org/10.3390/photochem1020010.

[129] A. Mau, C. Dietlin, F. Dumur, J. Lalevée, Concomitant initiation of radical and cationic polymerisations using new copper complexes as photoinitiators: Synthesis and characterisation of acrylate/epoxy interpenetrated polymer networks, Eur. Polym. J. 152 (2021) 110457. https://doi.org/10.1016/j.eurpolymj.2021.110457.

[130] P. Garra, F. Dumur, D. Gigmes, A. Al Mousawi, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, Copper (Photo)redox Catalyst for Radical Photopolymerization in Shadowed Areas and Access to Thick and Filled Samples, Macromolecules. 50 (2017) 3761–3771. https://doi.org/10.1021/acs.macromol.7b00622.

[131] P. Garra, F. Dumur, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, A New Highly Efficient Amine-Free and Peroxide-Free Redox System for Free Radical Polymerization under Air with Possible Light Activation, Macromolecules. 49 (2016) 6296–6309. https://doi.org/10.1021/acs.macromol.6b01615.

[132] P. Garra, A. Kermagoret, A.A. Mousawi, F. Dumur, D. Gigmes, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, New copper(I) complex based initiating systems in redox polymerization and comparison with the amine/benzoyl peroxide reference, Polym. Chem. 8 (2017) 4088–4097. https://doi.org/10.1039/C7PY00726D.

[133] G. Noirbent, F. Dumur, Recent Advances on Copper Complexes as Visible Light Photoinitiators and (Photo) Redox Initiators of Polymerization, Catalysts. 10 (2020). https://doi.org/10.3390/catal10090953.

[134] T. Borjigin, G. Noirbent, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, The new LED-Sensitive photoinitiators of Polymerization: Copper complexes in free radical and cationic photoinitiating systems and application in 3D printing, Eur. Polym. J. 162 (2022) 110885. https://doi.org/10.1016/j.eurpolymj.2021.110885.

[135] M. Rahal, G. Noirbent, B. Graff, J. Toufaily, T. Hamieh, D. Gigmes, F. Dumur, J. Lalevée, Novel Copper Complexes as Visible Light Photoinitiators for the Synthesis of Interpenetrating Polymer Networks (IPNs), Polymers. 14 (2022). https://doi.org/10.3390/polym14101998.

[136] J.-T. Lin, J. Lalevee, D.-C. Cheng, Efficacy analysis of new copper complex for visible light (455, 530 nm) radical/cationic photopolymerization: The synergic effects and catalytic cycle, PLOS ONE. 17 (2022) e0270679. https://doi.org/10.1371/journal.pone.0270679.

[137] F. Dumur, Recent Advances on Visible Light Thiophene-based Photoinitiators of Polymerization, Eur. Polym. J. (2022) 111120. https://doi.org/10.1016/j.eurpolymj.2022.111120.

[138] M.-A. Tehfe, F. Dumur, E. Contal, B. Graff, D. Gigmes, J.-P. Fouassier, J. Lalevée, Novel Highly Efficient Organophotocatalysts: Truxene–Acridine-1,8-diones as Photoinitiators of Polymerization, Macromol. Chem. Phys. 214 (2013) 2189–2201. https://doi.org/10.1002/macp.201300362.

[139] P. Xiao, F. Dumur, M.-A. Tehfe, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Difunctional acridinediones as photoinitiators of polymerization under UV and visible lights: Structural effects, Polymer. 54 (2013) 3458–3466. https://doi.org/10.1016/j.polymer.2013.04.055.

[140] P. Xiao, F. Dumur, M.-A. Tehfe, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Acridinediones: Effect of Substituents on Their Photoinitiating Abilities in Radical and Cationic Photopolymerization, Macromol. Chem. Phys. 214 (2013) 2276–2282. https://doi.org/10.1002/macp.201300363.

[141] M.-A. Tehfe, F. Dumur, P. Xiao, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gigmes, J. Lalevée, New chromone based photoinitiators for polymerization reactions under visible light, Polym. Chem. 4 (2013) 4234–4244. https://doi.org/10.1039/C3PY00536D.

[142] J. You, H. Fu, D. Zhao, T. Hu, J. Nie, T. Wang, Flavonol dyes with different substituents in photopolymerization, J. Photochem. Photobiol. Chem. 386 (2020) 112097. https://doi.org/10.1016/j.jphotochem.2019.112097.

[143] A. Al Mousawi, P. Garra, M. Schmitt, J. Toufaily, T. Hamieh, B. Graff, J.P. Fouassier, F. Dumur, J. Lalevée, 3-Hydroxyflavone and N-Phenylglycine in High Performance Photoinitiating Systems for 3D Printing and Photocomposites Synthesis, Macromolecules. 51 (2018) 4633–4641. https://doi.org/10.1021/acs.macromol.8b00979.

[144] M. Ghali, M. Benltifa, C. Brahmi, L. Elbassi, F. Dumur, C. Simonnet-Jégat, L. Bousselmi, J. Lalevée, LED and solar photodecomposition of erythrosine B and rose Bengal using H3PMo12O40/polymer photocatalyst, Eur. Polym. J. 159 (2021) 110743. https://doi.org/10.1016/j.eurpolymj.2021.110743.

[145] C. Brahmi, M. Benltifa, M. Ghali, F. Dumur, C. Simonnet-Jégat, M. Valérie, F. Morlet-Savary, L. Bousselmi, J. Lalevée, Performance improvement of the photocatalytic process for the degradation of pharmaceutical compounds using new POM/polymer photocatalysts, J. Environ. Chem. Eng. 9 (2021) 106015. https://doi.org/10.1016/j.jece.2021.106015.

[146] C. Brahmi, M. Benltifa, M. Ghali, F. Dumur, C. Simonnet-Jégat, V. Monnier, F. Morlet-Savary, L. Bousselmi, J. Lalevée, Polyoxometalates/polymer composites for the photodegradation of bisphenol-A, J. Appl. Polym. Sci. 138 (2021) 50864. https://doi.org/10.1002/app.50864.

[147] C. Brahmi, M. Benltifa, C. Vaulot, L. Michelin, F. Dumur, A. Airoudj, F. Morlet-Savary, B. Raveau, L. Bousselmi, J. Lalevée, New hybrid perovskites/polymer composites for the photodegradation of organic dyes, Eur. Polym. J. 157 (2021) 110641. https://doi.org/10.1016/j.eurpolymj.2021.110641.

[148] H. Mokbel, F. Dumur, B. Raveau, F. Morlet-Savary, C. Simonnet-Jégat, D. Gigmes, J. Toufaily, T. Hamieh, J.P. Fouassier, J. Lalevée, Perovskites as new radical photoinitiators for radical and cationic polymerizations, Org. Chem. More Radic. Ever Before. 72 (2016) 7686–7690. https://doi.org/10.1016/j.tet.2016.03.057.

[149] M.-A. Tehfe, F. Dumur, E. Contal, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, New insights into radical and cationic polymerizations upon visible light exposure: role of novel photoinitiator systems based on the pyrene chromophore, Polym. Chem. 4 (2013) 1625–1634. https://doi.org/10.1039/C2PY20950K.

[150] S. Telitel, F. Dumur, T. Faury, B. Graff, M.-A. Tehfe, D. Gigmes, J.-P. Fouassier, J. Lalevée, New core-pyrene π structure organophotocatalysts usable as highly efficient photoinitiators, Beilstein J. Org. Chem. 9 (2013) 877–890. https://doi.org/10.3762/bjoc.9.101.

[151] N. Uchida, H. Nakano, T. Igarashi, T. Sakurai, Nonsalt 1-(arylmethyloxy)pyrene photoinitiators capable of initiating cationic polymerization, J. Appl. Polym. Sci. 131 (2014). https://doi.org/10.1002/app.40510.

[152] A. Mishra, S. Daswal, 1-(Bromoacetyl)pyrene, a novel photoinitiator for the copolymerization of styrene and methylmethacrylate, Radiat. Phys. Chem. 75 (2006) 1093–1100. https://doi.org/10.1016/j.radphyschem.2006.01.013.

[153] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, Design of new Type I and Type II photoinitiators possessing highly coupled pyrene–ketone moieties, Polym. Chem. 4 (2013) 2313–2324. https://doi.org/10.1039/C3PY21079K.

[154] F. Dumur, Recent advances on pyrene-based photoinitiators of polymerization, Eur. Polym. J. 126 (2020) 109564. https://doi.org/10.1016/j.eurpolymj.2020.109564.

[155] M.-A. Tehfe, F. Dumur, N. Vilà, B. Graff, C.R. Mayer, J.P. Fouassier, D. Gigmes, J. Lalevée, A Multicolor Photoinitiator for Cationic Polymerization and Interpenetrated Polymer Network Synthesis: 2,7-Di-tert-butyldimethyldihydropyrene, Macromol. Rapid Commun. 34 (2013) 1104–1109. https://doi.org/10.1002/marc.201300302.

[156] S. Telitel, F. Dumur, D. Gigmes, B. Graff, J.P. Fouassier, J. Lalevée, New functionalized aromatic ketones as photoinitiating systems for near visible and visible light induced polymerizations, Polymer. 54 (2013) 2857–2864. https://doi.org/10.1016/j.polymer.2013.03.062.

[157] M.-A. Tehfe, J. Lalevée, S. Telitel, E. Contal, F. Dumur, D. Gigmes, D. Bertin, M. Nechab, B. Graff, F. Morlet-Savary, J.-P. Fouassier, Polyaromatic Structures as Organo-Photoinitiator Catalysts for Efficient Visible Light Induced Dual Radical/Cationic Photopolymerization and Interpenetrated Polymer Networks Synthesis, Macromolecules. 45 (2012) 4454–4460. https://doi.org/10.1021/ma300760c.

[158] M.-A. Tehfe, F. Dumur, B. Graff, J.-L. Clément, D. Gigmes, F. Morlet-Savary, J.-P. Fouassier, J. Lalevée, New Cleavable Photoinitiator Architecture with Huge Molar Extinction Coefficients for Polymerization in the 340–450 nm Range., Macromolecules. 46 (2013) 736–746. https://doi.org/10.1021/ma3024359.

[159] J. Zhang, P. Xiao, F. Dumur, C. Guo, W. Hong, Y. Li, D. Gigmes, B. Graff, J.-P. Fouassier, J. Lalevée, Polymeric Photoinitiators: A New Search toward High Performance Visible Light Photoinitiating Systems, Macromol. Chem. Phys. 217 (2016) 2145–2153. https://doi.org/10.1002/macp.201600260.

[160] N. Zivic, M. Bouzrati-Zerrelli, S. Villotte, F. Morlet-Savary, C. Dietlin, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, A novel naphthalimide scaffold based iodonium salt as a one-component photoacid/photoinitiator for cationic and radical polymerization

under LED exposure, Polym. Chem. 7 (2016) 5873–5879. https://doi.org/10.1039/C6PY01306F.

[161] H. Mokbel, J. Toufaily, T. Hamieh, F. Dumur, D. Campolo, D. Gigmes, J.P. Fouassier, J. Ortyl, J. Lalevée, Specific cationic photoinitiators for near UV and visible LEDs: Iodonium versus ferrocenium structures, J. Appl. Polym. Sci. 132 (2015) 42759. https://doi.org/10.1002/app.42759.

[162] S. Villotte, D. Gigmes, F. Dumur, J. Lalevée, Design of Iodonium Salts for UV or Near-UV LEDs for Photoacid Generator and Polymerization Purposes, Molecules. 25 (2020) 149. https://doi.org/10.3390/molecules25010149.

[163] M.A. Tasdelen, V. Kumbaraci, S. Jockusch, N.J. Turro, N. Talinli, Y. Yagci, Photoacid Generation by Stepwise Two-Photon Absorption: Photoinitiated Cationic Polymerization of Cyclohexene Oxide by Using Benzodioxinone in the Presence of Iodonium Salt, Macromolecules. 41 (2008) 295–297. https://doi.org/10.1021/ma7023649.

[164] J.V. Crivello, J.H.W. Lam, Diaryliodonium Salts. A New Class of Photoinitiators for Cationic Polymerization, Macromolecules. 10 (1977) 1307–1315. https://doi.org/10.1021/ma60060a028.

[165] Y. He, W. Zhou, F. Wu, M. Li, E. Wang, Photoreaction and photopolymerization studies on squaraine dyes/iodonium salts combination, J. Photochem. Photobiol. Chem. 162 (2004) 463–471. https://doi.org/10.1016/S1010-6030(03)00390-3.

[166] L.I. Jun, L.I. Miaozhen, S. Huaihai, Y. Yongyuan, W. Erjian, Photopolymerization Initiated by Dimethylaminochalcone/Diphenyliodonium Salt Combination System Sensitive to Visible Light, Chin. J Polym Sci. 11 (1993) 163–170.

[167] N. Zivic, P.K. Kuroishi, F. Dumur, D. Gigmes, A.P. Dove, H. Sardon, Recent Advances and Challenges in the Design of Organic Photoacid and Photobase Generators for Polymerizations, Angew. Chem. Int. Ed. 58 (2019) 10410–10422. https://doi.org/10.1002/anie.201810118.

[168] H. Chen, G. Noirbent, K. Sun, D. Brunel, D. Gigmes, F. Morlet-Savary, Y. Zhang, S. Liu, P. Xiao, F. Dumur, J. Lalevée, Photoinitiators derived from natural product scaffolds: monochalcones in three-component photoinitiating systems and their applications in 3D printing, Polym. Chem. 11 (2020) 4647–4659. https://doi.org/10.1039/D0PY00568A.

[169] L. Tang, J. Nie, X. Zhu, A high performance phenyl-free LED photoinitiator for cationic or hybrid photopolymerization and its application in LED cationic 3D printing, Polym. Chem. 11 (2020) 2855–2863. https://doi.org/10.1039/D0PY00142B.

[170] Y. Xu, G. Noirbent, D. Brunel, Z. Ding, D. Gigmes, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Allyloxy ketones as efficient photoinitiators with high migration stability in free radical polymerization and 3D printing, Dyes Pigments. 185 (2021) 108900. https://doi.org/10.1016/j.dyepig.2020.108900.

[171] Y. Xu, Z. Ding, H. Zhu, B. Graff, S. Knopf, P. Xiao, F. Dumur, J. Lalevée, Design of ketone derivatives as highly efficient photoinitiators for free radical and cationic photopolymerizations and application in 3D printing of composites, J. Polym. Sci. 58 (2020) 3432–3445. https://doi.org/10.1002/pol.20200658.

[172] H. Chen, G. Noirbent, S. Liu, D. Brunel, B. Graff, D. Gigmes, Y. Zhang, K. Sun, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, Bis-chalcone derivatives derived from natural products as near-UV/visible light sensitive photoinitiators for 3D/4D printing, Mater. Chem. Front. 5 (2021) 901–916. https://doi.org/10.1039/D0QM00755B.

[173] S. Liu, Y. Zhang, K. Sun, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Design of photoinitiating systems based on the chalcone-anthracene scaffold for LED cationic

photopolymerization and application in 3D printing, Eur. Polym. J. 147 (2021) 110300. https://doi.org/10.1016/j.eurpolymj.2021.110300.

[174] N. Giacoletto, F. Dumur, Recent Advances in bis-Chalcone-Based Photoinitiators of Polymerization: From Mechanistic Investigations to Applications, Molecules. 26 (2021) 3192. https://doi.org/10.3390/molecules26113192.

[175] M. Ibrahim-Ouali, F. Dumur, Recent Advances on Chalcone-based Photoinitiators of Polymerization, Eur. Polym. J. (2021) 110688. https://doi.org/10.1016/j.eurpolymj.2021.110688.

[176] H. Chen, G. Noirbent, S. Liu, Y. Zhang, K. Sun, F. Morlet-Savary, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, In situ generation of Ag nanoparticles during photopolymerization by using newly developed dyes-based three-component photoinitiating systems and the related 3D printing applications and their shape change behavior, J. Polym. Sci. 59 (2021) 843–859. https://doi.org/10.1002/pol.20210154.

[177] H. Chen, M. Vahdati, P. Xiao, F. Dumur, J. Lalevée, Water-Soluble Visible Light Sensitive Photoinitiating System Based on Charge Transfer Complexes for the 3D Printing of Hydrogels, Polymers. 13 (2021). https://doi.org/10.3390/polym13183195.

[178] M.-A. Tehfe, F. Dumur, P. Xiao, M. Delgove, B. Graff, J.-P. Fouassier, D. Gigmes, J. Lalevée, Chalcone derivatives as highly versatile photoinitiators for radical, cationic, thiol–ene and IPN polymerization reactions upon exposure to visible light, Polym. Chem. 5 (2014) 382–390. https://doi.org/10.1039/C3PY00922J.

[179] K. Sun, Y. Xu, F. Dumur, F. Morlet-Savary, H. Chen, C. Dietlin, B. Graff, J. Lalevée, P. Xiao, In silico rational design by molecular modeling of new ketones as photoinitiators in three-component photoinitiating systems: application in 3D printing, Polym. Chem. 11 (2020) 2230–2242. https://doi.org/10.1039/C9PY01874C.

[180] H. Chen, C. Regeard, H. Salmi, F. Morlet-Savary, N. Giacoletto, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, Interpenetrating polymer network hydrogels using natural based dyes initiating systems: antibacterial activity and 3D/4D performance, Eur. Polym. J. (2022) 111042. https://doi.org/10.1016/j.eurpolymj.2022.111042.

[181] H. Mokbel, F. Dumur, J. Lalevée, On demand NIR activated photopolyaddition reactions, Polym. Chem. 11 (2020) 4250–4259. https://doi.org/10.1039/D0PY00639D.

[182] H. Mokbel, B. Graff, F. Dumur, J. Lalevée, NIR Sensitizer Operating under Long Wavelength (1064 nm) for Free Radical Photopolymerization Processes, Macromol. Rapid Commun. 41 (2020) 2000289. https://doi.org/10.1002/marc.202000289.

[183] V. Launay, F. Dumur, D. Gigmes, J. Lalevée, Near-infrared light for polymer re-shaping and re-processing applications, J. Polym. Sci. 59 (2021) 2193–2200. https://doi.org/10.1002/pol.20210450.

[184] A. Caron, G. Noirbent, D. Gigmes, F. Dumur, J. Lalevée, Near-Infrared PhotoInitiating Systems: Photothermal versus Triplet–Triplet Annihilation-Based Upconversion Polymerization, Macromol. Rapid Commun. 42 (2021) 2100047. https://doi.org/10.1002/marc.202100047.

[185] A.-H. Bonardi, F. Bonardi, F. Morlet-Savary, C. Dietlin, G. Noirbent, T.M. Grant, J.-P. Fouassier, F. Dumur, B.H. Lessard, D. Gigmes, J. Lalevée, Photoinduced Thermal Polymerization Reactions, Macromolecules. 51 (2018) 8808–8820. https://doi.org/10.1021/acs.macromol.8b01741.

[186] V. Launay, F. Dumur, L. Pieuchot, J. Lalevée, Safe near infrared light for fast polymers surface sterilization using organic heaters, Mater. Chem. Front. 6 (2022) 1172–1179. https://doi.org/10.1039/D1QM01609A.

[187] V. Launay, R. Wolf, F. Dumur, J. Lalevée, Photothermal activation in the near infrared range for 4-dimensional printing using relevant organic dyes, Addit. Manuf. 58 (2022) 103031. https://doi.org/10.1016/j.addma.2022.103031.

[188] J. Lalevée, F. Dumur, M.-A. Tehfe, A. Zein-Fakih, D. Gigmes, F. Morlet-Savary, B. Graff, J.-P. Fouassier, Dye photosensitized cationic ring-opening polymerization: Search for new dye skeletons, Polymer. 53 (2012) 4947–4954. https://doi.org/10.1016/j.polymer.2012.08.067.

[189] N. Karaca, N. Ocal, N. Arsu, S. Jockusch, Thioxanthone-benzothiophenes as photoinitiator for free radical polymerization, J. Photochem. Photobiol. Chem. 331 (2016) 22–28. https://doi.org/10.1016/j.jphotochem.2016.01.017.

[190] D.K. Balta, N. Cetiner, G. Temel, Z. Turgut, N. Arsu, An annelated thioxanthone as a new Type II initiator, J. Photochem. Photobiol. Chem. 199 (2008) 316–321. https://doi.org/10.1016/j.jphotochem.2008.06.008.

[191] D.K. Balta, G. Temel, G. Goksu, N. Ocal, N. Arsu, Thioxanthone–Diphenyl Anthracene: Visible Light Photoinitiator, Macromolecules. 45 (2012) 119–125. https://doi.org/10.1021/ma202168m.

[192] S. Dadashi-Silab, C. Aydogan, Y. Yagci, Shining a light on an adaptable photoinitiator: advances in photopolymerizations initiated by thioxanthones, Polym. Chem. 6 (2015) 6595–6615. https://doi.org/10.1039/C5PY01004G.

[193] T.N. Eren, N. Yasar, V. Aviyente, F. Morlet-Savary, B. Graff, J.P. Fouassier, J. Lalevee, D. Avci, Photophysical and Photochemical Studies of Novel Thioxanthone-Functionalized Methacrylates through LED Excitation, Macromol. Chem. Phys. 217 (2016) 1501–1512. https://doi.org/10.1002/macp.201600051.

[194] J. Qiu, J. Wei, Thioxanthone photoinitiator containing polymerizable N-aromatic maleimide for photopolymerization, J. Polym. Res. 21 (2014) 559. https://doi.org/10.1007/s10965-014-0559-4.

[195] H. Tar, D. Sevinc Esen, M. Aydin, C. Ley, N. Arsu, X. Allonas, Panchromatic Type II Photoinitiator for Free Radical Polymerization Based on Thioxanthone Derivative, Macromolecules. 46 (2013) 3266–3272. https://doi.org/10.1021/ma302641d.

[196] Q. Wu, X. Wang, Y. Xiong, J. Yang, H. Tang, Thioxanthone based one-component polymerizable visible light photoinitiator for free radical polymerization, RSC Adv. 6 (2016) 66098–66107. https://doi.org/10.1039/C6RA15349F.

[197] Q. Wu, K. Tang, Y. Xiong, X. Wang, J. Yang, H. Tang, High-Performance and Low Migration One-Component Thioxanthone Visible Light Photoinitiators, Macromol. Chem. Phys. 218 (2017) 1600484. https://doi.org/10.1002/macp.201600484.

[198] X. Wu, M. Jin, J.-P. Malval, D. Wan, H. Pu, Visible light-emitting diode-sensitive thioxanthone derivatives used in versatile photoinitiating systems for photopolymerizations, J. Polym. Sci. Part Polym. Chem. 55 (2017) 4037–4045. https://doi.org/10.1002/pola.28871.

[199] J. Lalevée, M.-A. Tehfe, F. Dumur, D. Gigmes, B. Graff, F. Morlet-Savary, J.-P. Fouassier, Light-Harvesting Organic Photoinitiators of Polymerization, Macromol. Rapid Commun. 34 (2013) 239–245. https://doi.org/10.1002/marc.201200578.

[200] D.S. Esen, F. Karasu, N. Arsu, The investigation of photoinitiated polymerization of multifunctional acrylates with TX-BT by Photo-DSC and RT-FTIR, Prog. Org. Coat. 70 (2011) 102–107. https://doi.org/10.1016/j.porgcoat.2010.10.010.

[201] J. Lalevée, N. Blanchard, M.A. Tehfe, C. Fries, F. Morlet-Savary, D. Gigmes, J.P. Fouassier, New thioxanthone and xanthone photoinitiators based on silyl radical chemistry, Polym. Chem. 2 (2011) 1077–1084. https://doi.org/10.1039/C0PY00392A.

[202] T. Gencoglu, T.N. Eren, J. Lalevée, D. Avci, A Water Soluble, Low Migration, and Visible Light Photoinitiator by Thioxanthone-Functionalization of Poly(ethylene glycol)-Containing Poly(β-amino ester), Macromol. Chem. Phys. n/a (2022) 2100450. https://doi.org/10.1002/macp.202100450.

[203] S. Telitel, F. Dumur, D. Campolo, J. Poly, D. Gigmes, J.P. Fouassier, J. Lalevée, Iron complexes as potential photocatalysts for controlled radical photopolymerizations: A tool for modifications and patterning of surfaces, J. Polym. Sci. Part Polym. Chem. 54 (2016) 702–713. https://doi.org/10.1002/pola.27896.

[204] J. Zhang, D. Campolo, F. Dumur, P. Xiao, J.P. Fouassier, D. Gigmes, J. Lalevée, Iron complexes as photoinitiators for radical and cationic polymerization through photoredox catalysis processes, J. Polym. Sci. Part Polym. Chem. 53 (2015) 42–49. https://doi.org/10.1002/pola.27435.

[205] J. Zhang, D. Campolo, F. Dumur, P. Xiao, J.P. Fouassier, D. Gigmes, J. Lalevée, Visible-light-sensitive photoredox catalysis by iron complexes: Applications in cationic and radical polymerization reactions, J. Polym. Sci. Part Polym. Chem. 54 (2016) 2247–2253. https://doi.org/10.1002/pola.28098.

[206] J. Zhang, D. Campolo, F. Dumur, P. Xiao, J.P. Fouassier, D. Gigmes, J. Lalevée, Iron Complexes in Visible-Light-Sensitive Photoredox Catalysis: Effect of Ligands on Their Photoinitiation Efficiencies, ChemCatChem. 8 (2016) 2227–2233. https://doi.org/10.1002/cctc.201600320.

[207] F. Dumur, Recent advances on ferrocene-based photoinitiating systems, Eur. Polym. J. 147 (2021) 110328. https://doi.org/10.1016/j.eurpolymj.2021.110328.

[208] F. Dumur, Recent advances on iron-based photoinitiators of polymerization, Eur. Polym. J. 139 (2020) 110026. https://doi.org/10.1016/j.eurpolymj.2020.110026.

[209] M. Topa-Skwarczyńska, M. Galek, M. Jankowska, F. Morlet-Savary, B. Graff, J. Lalevée, R. Popielarz, J. Ortyl, Development of the first panchromatic BODIPY-based one-component iodonium salts for initiating the photopolymerization processes, Polym. Chem. 12 (2021) 6873–6893. https://doi.org/10.1039/D1PY01263K.

[210] Y. Xu, T. Feng, T. Yang, H. Wei, H. Yang, G. Li, M. Zhao, S. Liu, W. Huang, Q. Zhao, Utilizing Intramolecular Photoinduced Electron Transfer to Enhance Photothermal Tumor Treatment of Aza-BODIPY-Based Near-Infrared Nanoparticles, ACS Appl. Mater. Interfaces. 10 (2018) 16299–16307. https://doi.org/10.1021/acsami.8b03568.

[211] A. Skotnicka, J. Kabatc, New BODIPY Dyes Based on Benzoxazole as Photosensitizers in Radical Polymerization of Acrylate Monomers, Materials. 15 (2022). https://doi.org/10.3390/ma15020662.

[212] P. Lu, K.-Y. Chung, A. Stafford, M. Kiker, K. Kafle, Z.A. Page, Boron dipyrromethene (BODIPY) in polymer chemistry, Polym. Chem. 12 (2021) 327–348. https://doi.org/10.1039/D0PY01513J.

[213] S. Telitel, N. Blanchard, S. Schweizer, F. Morlet-Savary, B. Graff, J.-P. Fouassier, J. Lalevée, BODIPY derivatives and boranil as new photoinitiating systems of cationic polymerization exhibiting a tunable absorption in the 400–600 nm spectral range, Polymer. 54 (2013) 2071–2076. https://doi.org/10.1016/j.polymer.2013.02.013.

[214] S. Telitel, J. Lalevée, N. Blanchard, T. Kavalli, M.-A. Tehfe, S. Schweizer, F. Morlet-Savary, B. Graff, J.-P. Fouassier, Photopolymerization of Cationic Monomers and

Acrylate/Divinylether Blends under Visible Light Using Pyrromethene Dyes, Macromolecules. 45 (2012) 6864–6868. https://doi.org/10.1021/ma301293m.

[215] J. Li, X. Zhang, S. Ali, M.Y. Akram, J. Nie, X. Zhu, The effect of polyethylene glycoldiacrylate complexation on type II photoinitiator and promotion for visible light initiation system, J. Photochem. Photobiol. Chem. 384 (2019) 112037. https://doi.org/10.1016/j.jphotochem.2019.112037.

[216] J. Li, S. Li, Y. Li, R. Li, J. Nie, X. Zhu, In situ monitoring of photopolymerization by photoinitiator with luminescence characteristics, J. Photochem. Photobiol. Chem. 389 (2020) 112225. https://doi.org/10.1016/j.jphotochem.2019.112225.

[217] J. Li, Y. Hao, M. Zhong, L. Tang, J. Nie, X. Zhu, Synthesis of furan derivative as LED light photoinitiator: One-pot, low usage, photobleaching for light color 3D printing, Dyes Pigments. 165 (2019) 467–473. https://doi.org/10.1016/j.dyepig.2019.03.011.

[218] Y. Xu, G. Noirbent, D. Brunel, Z. Ding, D. Gigmes, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Novel ketone derivative-based photoinitiating systems for free radical polymerization under mild conditions and 3D printing, Polym. Chem. 11 (2020) 5767–5777. https://doi.org/10.1039/D0PY00990C.

[219] F. Dumur, Recent advances on benzylidene ketones as photoinitiators of polymerization, Eur. Polym. J. 178 (2022) 111500. https://doi.org/10.1016/j.eurpolymj.2022.111500.

[220] Y. Zhao, W. Wang, F. Wu, Y. Zhou, N. Huang, Y. Gu, Q. Zou, W. Yang, Polyethylene glycol-functionalized benzylidene cyclopentanone dyes for two-photon excited photodynamic therapy, Org. Biomol. Chem. 9 (2011) 4168–4175. https://doi.org/10.1039/C0OB01278E.

[221] Y. Fang, T. Liu, Q. Zou, Y. Zhao, F. Wu, Cationic benzylidene cyclopentanone photosensitizers for selective photodynamic inactivation of bacteria over mammalian cells, RSC Adv. 5 (2015) 56067–56074. https://doi.org/10.1039/C5RA06143A.

[222] J. Xue, Y. Zhao, F. Wu, D.-C. Fang, Effect of Bridging Position on the Two-Photon Polymerization Initiating Efficiencies of Novel Coumarin/Benzylidene Cyclopentanone Dyes, J. Phys. Chem. A. 114 (2010) 5171–5179. https://doi.org/10.1021/jp909745q.

[223] J. Zhang, D. Campolo, F. Dumur, P. Xiao, D. Gigmes, J.P. Fouassier, J. Lalevée, The carbazole-bound ferrocenium salt as a specific cationic photoinitiator upon near-UV and visible LEDs (365–405 nm), Polym. Bull. 73 (2016) 493–507. https://doi.org/10.1007/s00289-015-1506-1.

[224] A. Al Mousawi, F. Dumur, P. Garra, J. Toufaily, T. Hamieh, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Carbazole Scaffold Based Photoinitiator/Photoredox Catalysts: Toward New High Performance Photoinitiating Systems and Application in LED Projector 3D Printing Resins, Macromolecules. 50 (2017) 2747–2758. https://doi.org/10.1021/acs.macromol.7b00210.

[225] A. Al Mousawi, D.M. Lara, G. Noirbent, F. Dumur, J. Toufaily, T. Hamieh, T.-T. Bui, F. Goubard, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Carbazole Derivatives with Thermally Activated Delayed Fluorescence Property as Photoinitiators/Photoredox Catalysts for LED 3D Printing Technology, Macromolecules. 50 (2017) 4913–4926. https://doi.org/10.1021/acs.macromol.7b01114.

[226] A. Al Mousawi, P. Garra, F. Dumur, T.-T. Bui, F. Goubard, J. Toufaily, T. Hamieh, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Novel Carbazole Skeleton-Based Photoinitiators for LED Polymerization and LED Projector 3D Printing, Molecules. 22 (2017) 2143. https://doi.org/10.3390/molecules22122143.

[227] A.A. Mousawi, A. Arar, M. Ibrahim-Ouali, S. Duval, F. Dumur, P. Garra, J. Toufaily, T. Hamieh, B. Graff, D. Gigmes, J.-P. Fouassier, J. Lalevée, Carbazole-based compounds as photoinitiators for free radical and cationic polymerization upon near visible light illumination, Photochem. Photobiol. Sci. 17 (2018) 578–585. https://doi.org/10.1039/C7PP00400A.

[228] M. Abdallah, D. Magaldi, A. Hijazi, B. Graff, F. Dumur, J.-P. Fouassier, T.-T. Bui, F. Goubard, J. Lalevée, Development of new high-performance visible light photoinitiators based on carbazole scaffold and their applications in 3d printing and photocomposite synthesis, J. Polym. Sci. Part Polym. Chem. 57 (2019) 2081–2092. https://doi.org/10.1002/pola.29471.

[229] F. Dumur, Recent advances on carbazole-based photoinitiators of polymerization, Eur. Polym. J. 125 (2020) 109503. https://doi.org/10.1016/j.eurpolymj.2020.109503.

[230] S. Liu, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Nitro-Carbazole Based Oxime Esters as Dual Photo/Thermal Initiators for 3D Printing and Composite Preparation, Macromol. Rapid Commun. 42 (2021) 2100207. https://doi.org/10.1002/marc.202100207.

[231] F. Hammoud, A. Hijazi, S. Duval, J. Lalevée, F. Dumur, 5,12-Dihydroindolo[3,2-a]carbazole: A promising scaffold for the design of visible light photoinitiators of polymerization, Eur. Polym. J. 162 (2022) 110880. https://doi.org/10.1016/j.eurpolymj.2021.110880.

[232] S. Liu, N. Giacoletto, M. Schmitt, M. Nechab, B. Graff, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, Effect of Decarboxylation on the Photoinitiation Behavior of Nitrocarbazole-Based Oxime Esters, Macromolecules. 55 (2022) 2475–2485. https://doi.org/10.1021/acs.macromol.2c00294.

[233] F. Hammoud, A. Hijazi, M. Ibrahim-Ouali, J. Lalevée, F. Dumur, Chemical engineering around the 5,12-dihydroindolo[3,2-a]carbazole scaffold : Fine tuning of the optical properties of visible light photoinitiators of polymerization, Eur. Polym. J. (2022) 111218. https://doi.org/10.1016/j.eurpolymj.2022.111218.

[234] C. Xu, S. Gong, X. Wu, Y. Wu, Q. Liao, Y. Xiong, Z. Li, H. Tang, High-efficient carbazole-based photo-bleachable dyes as free radical initiators for visible light polymerization, Dyes Pigments. 198 (2022) 110039. https://doi.org/10.1016/j.dyepig.2021.110039.

[235] F. Dumur, Recent advances on carbazole-based oxime esters as photoinitiators of polymerization, Eur. Polym. J. 175 (2022) 111330. https://doi.org/10.1016/j.eurpolymj.2022.111330.

[236] F. Hammoud, N. Giacoletto, M. Nechab, B. Graff, A. Hijazi, F. Dumur, J. Lalevée, 5,12-Dialkyl-5,12-dihydroindolo[3,2-a]carbazole-Based Oxime-Esters for LED Photoinitiating Systems and Application on 3D Printing, Macromol. Mater. Eng. n/a (2022) 2200082. https://doi.org/10.1002/mame.202200082.

[237] S. Liu, H. Chen, Y. Zhang, K. Sun, Y. Xu, F. Morlet-Savary, B. Graff, G. Noirbent, C. Pigot, D. Brunel, M. Nechab, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, Monocomponent Photoinitiators based on Benzophenone-Carbazole Structure for LED Photoinitiating Systems and Application on 3D Printing, Polymers. 12 (2020) 1394. https://doi.org/10.3390/polym12061394.

[238] P. Xiao, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Variations on the Benzophenone Skeleton: Novel High Performance Blue Light Sensitive Photoinitiating Systems, Macromolecules. 46 (2013) 7661–7667. https://doi.org/10.1021/ma401766v.

[239] J. Zhang, M. Frigoli, F. Dumur, P. Xiao, L. Ronchi, B. Graff, F. Morlet-Savary, J.P. Fouassier, D. Gigmes, J. Lalevée, Design of Novel Photoinitiators for Radical and Cationic Photopolymerizations under Near UV and Visible LEDs (385, 395, and 405 nm)., Macromolecules. 47 (2014) 2811–2819. https://doi.org/10.1021/ma500612x.

[240] S. Liu, D. Brunel, G. Noirbent, A. Mau, H. Chen, F. Morlet-Savary, B. Graff, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, New multifunctional benzophenone-based photoinitiators with high migration stability and their applications in 3D printing, Mater. Chem. Front. 5 (2021) 1982–1994. https://doi.org/10.1039/D0QM00885K.

[241] S. Liu, D. Brunel, K. Sun, Y. Zhang, H. Chen, P. Xiao, F. Dumur, J. Lalevée, Novel Photoinitiators Based on Benzophenone-Triphenylamine Hybrid Structure for LED Photopolymerization, Macromol. Rapid Commun. 41 (2020) 2000460. https://doi.org/10.1002/marc.202000460.

[242] S. Liu, D. Brunel, K. Sun, Y. Xu, F. Morlet-Savary, B. Graff, P. Xiao, F. Dumur, J. Lalevée, A monocomponent bifunctional benzophenone–carbazole type II photoinitiator for LED photoinitiating systems, Polym. Chem. 11 (2020) 3551–3556. https://doi.org/10.1039/D0PY00644K.

[243] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gigmes, J. Lalevée, Trifunctional Photoinitiators Based on a Triazine Skeleton for Visible Light Source and UV LED Induced Polymerizations, Macromolecules. 45 (2012) 8639–8647. https://doi.org/10.1021/ma301931p.

[244] J.-T. Lin, J. Lalevee, Efficacy Modeling of New Multi-Functional Benzophenone-Based System for Free-Radical/Cationic Hybrid Photopolymerization Using 405 nm LED, (2021). https://doi.org/10.20944/preprints202106.0502.v1.

[245] F. Dumur, Recent advances on visible light pyrrole-derived photoinitiators of polymerization, Eur. Polym. J. 173 (2022) 111254. https://doi.org/10.1016/j.eurpolymj.2022.111254.

[246] F. Dumur, Recent Advances on Anthracene-based Photoinitiators of Polymerization, Eur. Polym. J. (2022) 111139. https://doi.org/10.1016/j.eurpolymj.2022.111139.

[247] M. Abdallah, H. Le, A. Hijazi, M. Schmitt, B. Graff, F. Dumur, T.-T. Bui, F. Goubard, J.-P. Fouassier, J. Lalevée, Acridone derivatives as high performance visible light photoinitiators for cationic and radical photosensitive resins for 3D printing technology and for low migration photopolymer property, Polymer. 159 (2018) 47–58. https://doi.org/10.1016/j.polymer.2018.11.021.

[248] J. Zhang, F. Dumur, M. Bouzrati, P. Xiao, C. Dietlin, F. Morlet-Savary, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Novel panchromatic photopolymerizable matrices: N,N′-dibutylquinacridone as an efficient and versatile photoinitiator, J. Polym. Sci. Part Polym. Chem. 53 (2015) 1719–1727. https://doi.org/10.1002/pola.27615.

[249] J. Lalevée, S. Telitel, M.A. Tehfe, J.P. Fouassier, D.P. Curran, E. Lacôte, N-Heterocyclic Carbene Boranes Accelerate Type I Radical Photopolymerizations and Overcome Oxygen Inhibition, Angew. Chem. Int. Ed. 51 (2012) 5958–5961.

[250] M.-A. Tehfe, F. Dumur, P. Xiao, J. Zhang, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, Photoinitiators based on a phenazine scaffold: High performance systems upon near-UV or visible LED (385, 395 and 405 nm) irradiations, Polymer. 55 (2014) 2285–2293. https://doi.org/10.1016/j.polymer.2014.04.005.

[251] F. Hammoud, A. Pavlou, A. Petropoulos, B. Graff, M.G. Siskos, A. Hijazi, F. Morlet-Savary, F. Dumur, J. Lalevée, Naphthoquinone-based imidazolyl esters as blue-light-

sensitive Type I photoinitiators, Polym. Chem. 13 (2022) 4817–4831. https://doi.org/10.1039/D2PY00753C.

[252] J. Kirschner, A. Baralle, J. Paillard, B. Graff, J.-M. Becht, J.E. Klee, J. Lalevée, Silyl Glyoximides: Toward a New Class of Visible Light Photoinitiators, Macromol. Chem. Phys. 223 (2022) 2100500. https://doi.org/10.1002/macp.202100500.

[253] Q. Ma, S. Liu, M. Le Dot, H. Mokbel, Y. Zhang, B. Graff, J. Lalevée, Imidazole based dual photo/thermal initiators for highly efficient radical polymerization under air with a metal-free approach, Polym. Chem. 12 (2021) 6386–6391. https://doi.org/10.1039/D1PY01079D.

[254] Q. Ma, L. Buchon, V. Magné, B. Graff, F. Morlet-Savary, Y. Xu, M. Benltifa, S. Lakhdar, J. Lalevée, Charge Transfer Complexes (CTCs) with Pyridinium Salts: Toward Efficient Dual Photochemical/Thermal Initiators and 3D Printing Applications, Macromol. Rapid Commun. n/a (2022) 2200314. https://doi.org/10.1002/marc.202200314.

[255] J. Zhang, J. Lalevée, J. Zhao, B. Graff, M.H. Stenzel, P. Xiao, Dihydroxyanthraquinone derivatives: natural dyes as blue-light-sensitive versatile photoinitiators of photopolymerization, Polym. Chem. 7 (2016) 7316–7324. https://doi.org/10.1039/C6PY01550F.

[256] A. Al Mousawi, C. Poriel, F. Dumur, J. Toufaily, T. Hamieh, J.P. Fouassier, J. Lalevée, Zinc Tetraphenylporphyrin as High Performance Visible Light Photoinitiator of Cationic Photosensitive Resins for LED Projector 3D Printing Applications, Macromolecules. 50 (2017) 746–753. https://doi.org/10.1021/acs.macromol.6b02596.

[257] G. Noirbent, Y. Xu, A.-H. Bonardi, D. Gigmes, J. Lalevée, F. Dumur, Metalated porphyrins as versatile visible light and NIR photoinitiators of polymerization, Eur. Polym. J. 139 (2020) 110019. https://doi.org/10.1016/j.eurpolymj.2020.110019.

[258] F. Dumur, Recent advances on visible light Triphenylamine-based photoinitiators of polymerization, Eur. Polym. J. 166 (2022) 111036. https://doi.org/10.1016/j.eurpolymj.2022.111036.

[259] D. Ladika, G. Noirbent, F. Dumur, D. Gigmes, A. Mourka, G.D. Barmparis, M. Farsari, D. Gray, Synthesis and application of triphenylamine-based aldehydes as photo-initiators for multi-photon lithography, Appl. Phys. A. 128 (2022) 745. https://doi.org/10.1007/s00339-022-05887-1.

[260] A.-H. Bonardi, S. Zahouily, C. Dietlin, B. Graff, F. Morlet-Savary, M. Ibrahim-Ouali, D. Gigmes, N. Hoffmann, F. Dumur, J. Lalevée, New 1,8-Naphthalimide Derivatives as Photoinitiators for Free-Radical Polymerization Upon Visible Light, Catalysts. 9 (2019) 637. https://doi.org/10.3390/catal9080637.

[261] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Naphthalimide-Tertiary Amine Derivatives as Blue-Light-Sensitive Photoinitiators, ChemPhotoChem. 2 (2018) 481–489. https://doi.org/10.1002/cptc.201800006.

[262] P. Xiao, F. Dumur, J. Zhang, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Naphthalimide Derivatives: Substituent Effects on the Photoinitiating Ability in Polymerizations under Near UV, Purple, White and Blue LEDs (385, 395, 405, 455, or 470 nm), Macromol. Chem. Phys. 216 (2015) 1782–1790. https://doi.org/10.1002/macp.201500150.

[263] P. Xiao, F. Dumur, J. Zhang, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Naphthalimide-phthalimide derivative based photoinitiating systems for polymerization reactions under blue lights, J. Polym. Sci. Part Polym. Chem. 53 (2015) 665–674. https://doi.org/10.1002/pola.27490.

[264] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, A benzophenone-naphthalimide derivative as versatile photoinitiator of polymerization under near UV and visible lights, J. Polym. Sci. Part Polym. Chem. 53 (2015) 445–451. https://doi.org/10.1002/pola.27451.

[265] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, N-[2-(Dimethylamino)ethyl]-1,8-naphthalimide derivatives as photoinitiators under LEDs, Polym. Chem. 9 (2018) 994–1003. https://doi.org/10.1039/C8PY00055G.

[266] J. Zhang, F. Dumur, P. Xiao, B. Graff, D. Bardelang, D. Gigmes, J.P. Fouassier, J. Lalevée, Structure Design of Naphthalimide Derivatives: Toward Versatile Photoinitiators for Near-UV/Visible LEDs, 3D Printing, and Water-Soluble Photoinitiating Systems, Macromolecules. 48 (2015) 2054–2063. https://doi.org/10.1021/acs.macromol.5b00201.

[267] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, UV-violet-blue LED induced polymerizations: Specific photoinitiating systems at 365, 385, 395 and 405 nm, Polymer. 55 (2014) 6641–6648. https://doi.org/10.1016/j.polymer.2014.11.002.

[268] P. Xiao, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Blue Light Sensitive Dyes for Various Photopolymerization Reactions: Naphthalimide and Naphthalic Anhydride Derivatives., Macromolecules. 47 (2014) 601–608. https://doi.org/10.1021/ma402376x.

[269] P. Xiao, F. Dumur, M. Frigoli, M.-A. Tehfe, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Naphthalimide based methacrylated photoinitiators in radical and cationic photopolymerization under visible light, Polym. Chem. 4 (2013) 5440–5448. https://doi.org/10.1039/C3PY00766A.

[270] G. Noirbent, F. Dumur, Recent advances on naphthalic anhydrides and 1,8-naphthalimide-based photoinitiators of polymerization, Eur. Polym. J. 132 (2020) 109702. https://doi.org/10.1016/j.eurpolymj.2020.109702.

[271] M. Rahal, H. Mokbel, B. Graff, V. Pertici, D. Gigmes, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, Naphthalimide-Based Dyes as Photoinitiators under Visible Light Irradiation and their Applications: Photocomposite Synthesis, 3D printing and Polymerization in Water, ChemPhotoChem. 5 (2021) 476–490. https://doi.org/10.1002/cptc.202000306.

[272] M. Rahal, B. Graff, J. Toufaily, T. Hamieh, M. Ibrahim-Ouali, F. Dumur, J. Lalevée, Naphthyl-Naphthalimides as High-Performance Visible Light Photoinitiators for 3D Printing and Photocomposites Synthesis, Catalysts. 11 (2021). https://doi.org/10.3390/catal11111269.

[273] N. Zivic, J. Zhang, D. Bardelang, F. Dumur, P. Xiao, T. Jet, D.-L. Versace, C. Dietlin, F. Morlet-Savary, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Novel naphthalimide–amine based photoinitiators operating under violet and blue LEDs and usable for various polymerization reactions and synthesis of hydrogels, Polym. Chem. 7 (2015) 418–429. https://doi.org/10.1039/C5PY01617G.

[274] P. Xiao, F. Dumur, B. Graff, F. Morlet-Savary, D. Gigmes, J.P. Fouassier, J. Lalevée, Design of High Performance Photoinitiators at 385–405 nm: Search around the Naphthalene Scaffold, Macromolecules. 47 (2014) 973–978. https://doi.org/10.1021/ma402622v.

[275] P. Xiao, F. Dumur, J. Zhang, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Amino and nitro substituted 2-amino-1H-benzo[de]isoquinoline-1,3(2H)-diones: as versatile photoinitiators of polymerization from violet-blue LED absorption to a panchromatic behavior, Polym. Chem. 6 (2015) 1171–1179. https://doi.org/10.1039/C4PY01409J.

[276] H. Chen, L. Pieuchot, P. Xiao, F. Dumur, J. Lalevée, Water-soluble/visible-light-sensitive naphthalimide derivative-based photoinitiating systems: 3D printing of antibacterial hydrogels, Polym. Chem. 13 (2022) 2918–2932. https://doi.org/10.1039/D2PY00417H.

[277] S. Liu, N. Giacoletto, B. Graff, F. Morlet-Savary, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, N-naphthalimide ester derivatives as Type I photoinitiators for LED photopolymerization, Mater. Today Chem. 26 (2022) 101137. https://doi.org/10.1016/j.mtchem.2022.101137.

[278] N. Giacoletto, M. Ibrahim-Ouali, F. Dumur, Recent advances on squaraine-based photoinitiators of polymerization, Eur. Polym. J. 150 (2021) 110427. https://doi.org/10.1016/j.eurpolymj.2021.110427.

[279] P. Xiao, F. Dumur, T.T. Bui, F. Goubard, B. Graff, F. Morlet-Savary, J.P. Fouassier, D. Gigmes, J. Lalevée, Panchromatic Photopolymerizable Cationic Films Using Indoline and Squaraine Dye Based Photoinitiating Systems, ACS Macro Lett. 2 (2013) 736–740. https://doi.org/10.1021/mz400316y.

[280] V. Launay, A. Caron, G. Noirbent, D. Gigmes, F. Dumur, J. Lalevée, NIR Organic Dyes as Innovative Tools for Reprocessing/Recycling of Plastics: Benefits of the Photothermal Activation in the Near-Infrared Range, Adv. Funct. Mater. 31 (2021) 2006324. https://doi.org/10.1002/adfm.202006324.

[281] A. Bonardi, F. Bonardi, G. Noirbent, F. Dumur, C. Dietlin, D. Gigmes, J.-P. Fouassier, J. Lalevée, Different NIR dye scaffolds for polymerization reactions under NIR light, Polym. Chem. 10 (2019) 6505–6514. https://doi.org/10.1039/C9PY01447K.

[282] A. Balcerak, D. Kwiatkowska, J. Kabatc, Novel photoinitiators based on difluoroborate complexes of squaraine dyes for radical polymerization of acrylates upon visible light, Polym. Chem. 13 (2022) 220–234. https://doi.org/10.1039/D1PY01294K.

[283] Q. Zou, H. Zhao, Y. Zhao, Y. Fang, D. Chen, J. Ren, X. Wang, Y. Wang, Y. Gu, F. Wu, Effective Two-Photon Excited Photodynamic Therapy of Xenograft Tumors Sensitized by Water-Soluble Bis(arylidene)cycloalkanone Photosensitizers, J. Med. Chem. 58 (2015) 7949–7958. https://doi.org/10.1021/acs.jmedchem.5b00731.

[284] Y. Fang, T. Liu, Q. Zou, Y. Zhao, F. Wu, Water-soluble benzylidene cyclopentanone based photosensitizers for in vitro and in vivo antimicrobial photodynamic therapy, Sci. Rep. 6 (2016) 28357. https://doi.org/10.1038/srep28357.

[285] S. Zhou, Z. Sun, Z. Ye, Y. Wang, L. Wang, L. Xing, H. Qiu, N. Huang, Y. Luo, Y. Zhao, Y. Gu, In vitro photodynamic inactivation effects of benzylidene cyclopentanone photosensitizers on clinical fluconazole-resistant Candida albicans, Photodiagnosis Photodyn. Ther. 22 (2018) 178–186. https://doi.org/10.1016/j.pdpdt.2018.04.001.

[286] M.V. Barnabas, A.D. Liu, A.D. Trifunac, V.V. Krongauz, C.T. Chang, Solvent effects on the photochemistry of a ketocyanine dye and its functional analog. Michler's ketone, J. Phys. Chem. 96 (1992) 212–217. https://doi.org/10.1021/j100180a041.

[287] K. Yamashita, S. Imahashi, S. Ito, Energy transfer and trap site formation in a photopolymer film containing carboxyl groups and benzylidene ketone dyes, Polymer. 44 (2003) 5573–5577. https://doi.org/10.1016/S0032-3861(03)00619-0.

[288] A.F.M.M. Rahman, R. Ali, Y. Jahng, A.A. Kadi, A Facile Solvent Free Claisen-Schmidt Reaction: Synthesis of α,α'-bis-(Substituted-benzylidene)cycloalkanones and α,α'-bis-(Substituted-alkylidene)cycloalkanones, Molecules. 17 (2012). https://doi.org/10.3390/molecules17010571.

[289] X.H. Cai, B. Xie, H. Guo, Synthesis of α,α'-bis(R-benzylidene)cycloalkanones catalyzed by potassium hydrogen sulfate under solvent-free conditions, Chem. Pap. 60 (2006) 318. https://doi.org/10.2478/s11696-006-0057-1.

[290] B.M. Monroe, W.K. Smothers, D.E. Keys, R.R. Krebs, D.J. Mickish, A.F. Harrington, S.R. Schicker, M.K. Armstrong, D.M.T. Chan, C.I. Weathers, Improved photopolymers for holographic recording. I, Imaging properties, J. Imaging Sci. 35 (1991) 19–25.

[291] E.-J. Wang, J. Li, Y.-Y. Yang, A new electron transfer sensitized initiation system for visible light induced photopolymerization: p-N,N-dimethylaminobenzal ketone/diphenyliodonium salt system, J. Photopolym. Sci. Technol. 4 (1991) 157–164. https://doi.org/10.2494/photopolymer.4.157.

[292] C. Belon, X. Allonas, C. Croutxé-barghorn, J. Lalevée, Overcoming the oxygen inhibition in the photopolymerization of acrylates: A study of the beneficial effect of triphenylphosphine, J. Polym. Sci. Part Polym. Chem. 48 (2010) 2462–2469. https://doi.org/10.1002/pola.24017.

[293] Z. Faraji Rad, P.D. Prewett, G.J. Davies, High-resolution two-photon polymerization: the most versatile technique for the fabrication of microneedle arrays, Microsyst. Nanoeng. 7 (2021) 71. https://doi.org/10.1038/s41378-021-00298-3.

[294] V. Harinarayana, Y.C. Shin, Two-photon lithography for three-dimensional fabrication in micro/nanoscale regime: A comprehensive review, Opt. Laser Technol. 142 (2021) 107180. https://doi.org/10.1016/j.optlastec.2021.107180.

[295] A.K. Nguyen, R.J. Narayan, Two-photon polymerization for biological applications, Mater. Today. 20 (2017) 314–322. https://doi.org/10.1016/j.mattod.2017.06.004.

[296] X. Zhou, Y. Hou, J. Lin, A review on the processing accuracy of two-photon polymerization, AIP Adv. 5 (2015) 030701. https://doi.org/10.1063/1.4916886.

[297] X. Huang, X. Wang, Y. Zhao, Study on a series of water-soluble photoinitiators for fabrication of 3D hydrogels by two-photon polymerization, Dyes Pigments. 141 (2017) 413–419. https://doi.org/10.1016/j.dyepig.2017.02.040.

[298] S. Maruo, O. Nakamura, S. Kawata, Three-dimensional microfabrication with two-photon-absorbed photopolymerization, Opt. Lett. 22 (1997) 132–134. https://doi.org/10.1364/OL.22.000132.

[299] A. Radke, T. Gissibl, T. Klotzbücher, P.V. Braun, H. Giessen, Three-Dimensional Bichiral Plasmonic Crystals Fabricated by Direct Laser Writing and Electroless Silver Plating, Adv. Mater. 23 (2011) 3018–3021. https://doi.org/10.1002/adma.201100543.

[300] N. Vasilantonakis, K. Terzaki, I. Sakellari, V. Purlys, D. Gray, C.M. Soukoulis, M. Vamvakaki, M. Kafesaki, M. Farsari, Three-Dimensional Metallic Photonic Crystals with Optical Bandgaps, Adv. Mater. 24 (2012) 1101–1105. https://doi.org/10.1002/adma.201104778.

[301] A.C. Henry, R.L. McCarley, Selective Deposition of Metals on Plastics Used in the Construction of Microanalytical Devices: Photo-Directed Formation of Metal Features on PMMA, J. Phys. Chem. B. 105 (2001) 8755–8761. https://doi.org/10.1021/jp011298y.

[302] J.K. Gansel, M. Thiel, M.S. Rill, M. Decker, K. Bade, V. Saile, G. von Freymann, S. Linden, M. Wegener, Gold Helix Photonic Metamaterial as Broadband Circular Polarizer, Science. 325 (2009) 1513–1515. https://doi.org/10.1126/science.1177031.

[303] M.T. Raimondi, S.M. Eaton, M. Laganà, V. Aprile, M.M. Nava, G. Cerullo, R. Osellame, Three-dimensional structural niches engineered via two-photon laser polymerization promote stem cell homing, Acta Biomater. 9 (2013) 4579–4584. https://doi.org/10.1016/j.actbio.2012.08.022.

[304] G. von Freymann, A. Ledermann, M. Thiel, I. Staude, S. Essig, K. Busch, M. Wegener, Three-Dimensional Nanostructures for Photonics, Adv. Funct. Mater. 20 (2010) 1038–1052. https://doi.org/10.1002/adfm.200901838.

[305] Z. Li, N. Pucher, K. Cicha, J. Torgersen, S.C. Ligon, A. Ajami, W. Husinsky, A. Rosspeintner, E. Vauthey, S. Naumov, T. Scherzer, J. Stampfl, R. Liska, A Straightforward Synthesis and Structure–Activity Relationship of Highly Efficient Initiators for Two-Photon Polymerization, Macromolecules. 46 (2013) 352–361. https://doi.org/10.1021/ma301770a.

[306] N. Pucher, A. Rosspeintner, V. Satzinger, V. Schmidt, G. Gescheidt, J. Stampfl, R. Liska, Structure−Activity Relationship in D-π-A-π-D-Based Photoinitiators for the Two-Photon-Induced Photopolymerization Process, Macromolecules. 42 (2009) 6519–6528. https://doi.org/10.1021/ma9007785.

[307] W.-E. Lu, X.-Z. Dong, W.-Q. Chen, Z.-S. Zhao, X.-M. Duan, Novel photoinitiator with a radical quenching moiety for confining radical diffusion in two-photon induced photopolymerization, J. Mater. Chem. 21 (2011) 5650–5659. https://doi.org/10.1039/C0JM04025H.

[308] C.N. LaFratta, J.T. Fourkas, T. Baldacchini, R.A. Farrer, Multiphoton Fabrication, Angew. Chem. Int. Ed. 46 (2007) 6238–6258. https://doi.org/10.1002/anie.200603995.

[309] S. Kawata, H.-B. Sun, T. Tanaka, K. Takada, Finer features for functional microdevices, Nature. 412 (2001) 697–698. https://doi.org/10.1038/35089130.

[310] H. Yuan, Y. Zhao, F. Wu, Two-Photon Acid Generation Systems Based on Dibenzylidene Ketone Dyes Intermolecular Sensitization, Chem. Mater. 24 (2012) 1371–1377. https://doi.org/10.1021/cm300148n.

[311] W. Zhou, S.M. Kuebler, K.L. Braun, T. Yu, J.K. Cammack, C.K. Ober, J.W. Perry, S.R. Marder, An Efficient Two-Photon-Generated Photoacid Applied to Positive-Tone 3D Microfabrication, Science. 296 (2002) 1106–1109. https://doi.org/10.1126/science.296.5570.1106.

[312] C.O. Yanez, C.D. Andrade, K.D. Belfield, Characterization of novel sulfonium photoacid generators and their microwave-assisted synthesis, Chem. Commun. (2009) 827–829. https://doi.org/10.1039/B815831B.

[313] M. Jin, H. Hong, J. Xie, J.-P. Malval, A. Spangenberg, O. Soppera, D. Wan, H. Pu, D.-L. Versace, T. Leclerc, P. Baldeck, O. Poizat, S. Knopf, π-conjugated sulfonium-based photoacid generators: an integrated molecular approach for efficient one and two-photon polymerization, Polym. Chem. 5 (2014) 4747–4755. https://doi.org/10.1039/C4PY00424H.

[314] K.D. Belfield, X. Ren, E.W. Van Stryland, D.J. Hagan, V. Dubikovsky, E.J. Miesak, Near-IR Two-Photon Photoinitiated Polymerization Using a Fluorone/Amine Initiating System, J. Am. Chem. Soc. 122 (2000) 1217–1218. https://doi.org/10.1021/ja991990v.

[315] M. Albota, D. Beljonne, J.-L. Brédas, J.E. Ehrlich, J.-Y. Fu, A.A. Heikal, S.E. Hess, T. Kogej, M.D. Levin, S.R. Marder, D. McCord-Maughon, J.W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W.W. Webb, X.-L. Wu, C. Xu, Design of Organic Molecules with Large Two-Photon Absorption Cross Sections, Science. 281 (1998) 1653–1656. https://doi.org/10.1126/science.281.5383.1653.

[316] D. Rehm, A. Weller, Kinetics of Fluorescence Quenching by Electron and H-Atom Transfer, Isr. J. Chem. 8 (1970) 259–271. https://doi.org/10.1002/ijch.197000029.

[317] D. Rehm, A. Weller, Kinetik und Mechanismus der Elektronübertragung bei der Fluoreszenzlöschung in Acetonitril, Berichte Bunsenges. Für Phys. Chem. 73 (1969) 834–839. https://doi.org/10.1002/bbpc.19690730818.

[318] J. Narewska, R. Strzelczyk, R. Podsiadły, Fluoflavin dyes as electron transfer photosensitizers for onium salt induced cationic photopolymerization, J. Photochem. Photobiol. Chem. 212 (2010) 68–74. https://doi.org/10.1016/j.jphotochem.2010.03.018.

[319] F. Ortica, J.C. Scaiano, G. Pohlers, J.F. Cameron, A. Zampini, Laser Flash Photolysis Study of Two Aromatic N-Oxyimidosulfonate Photoacid Generators, Chem. Mater. 12 (2000) 414–420. https://doi.org/10.1021/cm990440t.

[320] S. Suzuki, X. Allonas, J.-P. Fouassier, T. Urano, S. Takahara, T. Yamaoka, Interaction mechanism in pyrromethene dye/photoacid generator photosensitive system for high-speed photopolymer, J. Photochem. Photobiol. Chem. 181 (2006) 60–66. https://doi.org/10.1016/j.jphotochem.2005.10.035.

[321] R. Devi, S.C. Murugavel, Synthesis, spectral, and thermal characterization of photoreactive epoxy resin containing cycloalkanone moiety in the main chain, J. Appl. Polym. Sci. 124 (2012) 58–66. https://doi.org/10.1002/app.35028.

[322] C. Schmidt, T. Scherzer, Monitoring of the shrinkage during the photopolymerization of acrylates using hyphenated photorheometry/near-infrared spectroscopy, J. Polym. Sci. Part B Polym. Phys. 53 (2015) 729–739. https://doi.org/10.1002/polb.23694.

[323] Y. Mori, A. Sudo, T. Endo, Effect of oligo(spiroorthocarbonate)s on the volume shrinkage of epoxides during crosslinking by sulfonium salt-initiated cationic polymerization of epoxides, J. Polym. Sci. Part Polym. Chem. 57 (2019) 1564–1568. https://doi.org/10.1002/pola.29420.

[324] M. Shirai, Photocrosslinkable polymers with degradable properties, Polym. J. 46 (2014) 859–865. https://doi.org/10.1038/pj.2014.79.

[325] E. Skliutas, M. Lebedevaite, E. Kabouraki, T. Baldacchini, J. Ostrauskaite, M. Vamvakaki, M. Farsari, S. Juodkazis, M. Malinauskas, Polymerization mechanisms initiated by spatio-temporally confined light, Nanophotonics. 10 (2021) 1211–1242. https://doi.org/10.1515/nanoph-2020-0551.

[326] G. Trusiano, A. Vitale, C. Bonneaud, D. Pugliese, S. Dalle Vacche, C. Joly-Duhamel, C.M. Friesen, R. Bongiovanni, Vinyl ethers and epoxides photoinduced copolymerization with perfluoropolyalkylether monomers, Colloid Polym. Sci. 299 (2021) 509–521. https://doi.org/10.1007/s00396-020-04723-3.

[327] Gangadhara, K. Kishore, Novel photocrosslinkable liquid-crystalline polymers: poly[bis(benzylidene)] esters, Macromolecules. 26 (1993) 2995–3003. https://doi.org/10.1021/ma00064a001.

[328] R.D. Morrison, R.N. Boyd, Organic Chemistry, Prentice Hall India: New Delhi, 1953.

[329] K. Yamashita, S. Imahashi, S. Ito, Synthesis of benzylideneketone dyes and their photochemical properties as a sensitizer for alkali-developable photopolymerization systems, Dyes Pigments. 76 (2008) 748–753. https://doi.org/10.1016/j.dyepig.2007.01.014.

[330] J.-F. Xing, W.-Q. Chen, X.-Z. Dong, T. Tanaka, X.-Y. Fang, X.-M. Duan, S. Kawata, Synthesis, optical and initiating properties of new two-photon polymerization initiators: 2,7-Bis(styryl)anthraquinone derivatives, J. Photochem. Photobiol. Chem. 189 (2007) 398–404. https://doi.org/10.1016/j.jphotochem.2007.03.002.

[331] B.H. Cumpston, S.P. Ananthavel, S. Barlow, D.L. Dyer, J.E. Ehrlich, L.L. Erskine, A.A. Heikal, S.M. Kuebler, I.-Y.S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.-L. Wu, S.R. Marder, J.W. Perry, Two-photon polymerization initiators for three-

dimensional optical data storage and microfabrication, Nature. 398 (1999) 51–54. https://doi.org/10.1038/17989.

[332] Q. Zou, Y. Zhao, N.S. Makarov, J. Campo, H. Yuan, D.-C. Fang, J.W. Perry, F. Wu, Effect of alicyclic ring size on the photophysical and photochemical properties of bis(arylidene)cycloalkanone compounds, Phys. Chem. Chem. Phys. 14 (2012) 11743–11752. https://doi.org/10.1039/C2CP41952A.

[333] M.A. El-Sayed, Spin—Orbit Coupling and the Radiationless Processes in Nitrogen Heterocyclics, J. Chem. Phys. 38 (1963) 2834–2838. https://doi.org/10.1063/1.1733610.

[334] P. Pokhilko, A.I. Krylov, Quantitative El-Sayed Rules for Many-Body Wave Functions from Spinless Transition Density Matrices, J. Phys. Chem. Lett. 10 (2019) 4857–4862. https://doi.org/10.1021/acs.jpclett.9b02120.

[335] E. Yu-Tzu Li, T.-Y. Jiang, Y. Chi, P.-T. Chou, Semi-quantitative assessment of the intersystem crossing rate: an extension of the El-Sayed rule to the emissive transition metal complexes, Phys. Chem. Chem. Phys. 16 (2014) 26184–26192. https://doi.org/10.1039/C4CP03540B.

[336] X. Huang, Y. Zhang, M. Shi, Y. Zhang, Y. Zhao, Study on a polymerizable visible light initiator for fabrication of biosafety materials, Polym. Chem. 10 (2019) 2273–2281. https://doi.org/10.1039/C9PY00173E.

[337] J.R. Choi, K.W. Yong, J.Y. Choi, A.C. Cowie, Recent advances in photo-crosslinkable hydrogels for biomedical applications, BioTechniques. 66 (2019) 40–53. https://doi.org/10.2144/btn-2018-0083.

[338] W.T. Han, T. Jang, S. Chen, L.S.H. Chong, H.-D. Jung, J. Song, Improved cell viability for large-scale biofabrication with photo-crosslinkable hydrogel systems through a dual-photoinitiator approach, Biomater. Sci. 8 (2020) 450–461. https://doi.org/10.1039/C9BM01347D.

[339] Y. Tang, Y. Zhang, J. Yang, J. Nie, Synthesis and characteristics of photopolymerized benzophenone, J. Polym. Sci. Part Polym. Chem. 55 (2017) 313–320. https://doi.org/10.1002/pola.28386.

[340] T.N. Eren, N. Okte, F. Morlet-Savary, J.P. Fouassier, J. Lalevee, D. Avci, One-component thioxanthone-based polymeric photoinitiators, J. Polym. Sci. Part Polym. Chem. 54 (2016) 3370–3378. https://doi.org/10.1002/pola.28227.

[341] A. Oesterreicher, M. Roth, D. Hennen, F.H. Mostegel, M. Edler, S. Kappaun, T. Griesser, Low migration type I photoinitiators for biocompatible thiol-ene formulations, Eur. Polym. J. 88 (2017) 393–402. https://doi.org/10.1016/j.eurpolymj.2016.10.040.

[342] Y. Chen, J. Loccufier, L. Vanmaele, E. Barriau, H. Frey, Novel Multifunctional Polymeric Photoinitiators and Photo-Coinitiators Derived from Hyperbranched Polyglycerol, Macromol. Chem. Phys. 208 (2007) 1694–1706. https://doi.org/10.1002/macp.200700086.

[343] J. Wang, J. Cheng, J. Liu, Y. Gao, F. Sun, Self-floating ability and initiating gradient photopolymerization of acrylamide aqueous solution of a water-soluble polysiloxane benzophenone photoinitiator, Green Chem. 15 (2013) 2457–2465. https://doi.org/10.1039/C3GC40704G.

[344] M. Pietrzak, A. Wrzyszczyński, Novel sulfur—containing benzophenone derivative as radical photoinitiator for photopolymerization, J. Appl. Polym. Sci. 122 (2011) 2604–2608. https://doi.org/10.1002/app.34390.

[345] P. Xiao, S. Shi, J. Nie, Synthesis and characterization of copolymerizable one-component type II photoinitiator, Polym. Adv. Technol. 19 (2008) 1305–1310. https://doi.org/10.1002/pat.1132.

[346] S.A. Cınar, M.N. Guven, T.N. Eren, B. Cesur, M. Aleksanyan, B. Dedeoglu, N. Okte, V. Aviyente, F. Morlet-Savary, J. Lalevée, D. Avci, Structure-reactivity relationships of novel monomeric photoinitiators, J. Photochem. Photobiol. Chem. 329 (2016) 77–87. https://doi.org/10.1016/j.jphotochem.2016.06.015.

[347] K. Wang, Y. Lu, P. Chen, J. Shi, H. Wang, Q. Yu, Novel one-component polymeric benzophenone photoinitiator containing poly (ethylene glycol) as hydrogen donor, Mater. Chem. Phys. 143 (2014) 1391–1395. https://doi.org/10.1016/j.matchemphys.2013.11.051.

[348] J. Yang, W. Liao, Y. Xiong, Q. Wu, X. Wang, Z. Li, H. Tang, Naphthalimide dyes: Polymerizable one-component visible light initiators, Dyes Pigments. 148 (2018) 16–24. https://doi.org/10.1016/j.dyepig.2017.08.053.

[349] J. Yang, W. Liao, Y. Xiong, X. Wang, Z. Li, H. Tang, A multifunctionalized macromolecular silicone-naphthalimide visible photoinitiator for free radical polymerization, Prog. Org. Coat. 115 (2018) 151–158. https://doi.org/10.1016/j.porgcoat.2017.11.010.

[350] C. Carapina da Silva, B.S. Pacheco, R.N. das Neves, M.S. Dié Alves, Â. Sena-Lopes, S. Moura, S. Borsuk, C.M.P. de Pereira, Antiparasitic activity of synthetic curcumin monocarbonyl analogues against Trichomonas vaginalis, Biomed. Pharmacother. 111 (2019) 367–377. https://doi.org/10.1016/j.biopha.2018.12.058.

[351] L.M. Deck, L.A. Hunsaker, T.A. Vander Jagt, L.J. Whalen, R.E. Royer, D.L. Vander Jagt, Activation of anti-oxidant Nrf2 signaling by enone analogues of curcumin, Eur. J. Med. Chem. 143 (2018) 854–865. https://doi.org/10.1016/j.ejmech.2017.11.048.

[352] S. Yin, X. Zheng, X. Yao, Y. Wang, D. Liao, Synthesis and Anticancer Activity of Mono-Carbonyl Analogues of Curcumin, J. Cancer Ther. 04 (2013) 113–123. https://doi.org/10.4236/jct.2013.41016.

[353] C. Zhao, Y. Cai, X. He, J. Li, L. Zhang, J. Wu, Y. Zhao, S. Yang, X. Li, W. Li, G. Liang, Synthesis and anti-inflammatory evaluation of novel mono-carbonyl analogues of curcumin in LPS-stimulated RAW 264.7 macrophages, Eur. J. Med. Chem. 45 (2010) 5773–5780. https://doi.org/10.1016/j.ejmech.2010.09.037.

[354] E.R. Zhiganshina, M.V. Arsenyev, D.A. Chubich, D.A. Kolymagin, A.V. Pisarenko, D.S. Burkatovsky, E.V. Baranov, A.G. Vitukhnovsky, A.N. Lobanov, R.P. Matital, D.Ya. Aleynik, S.A. Chesnokov, Tetramethacrylic benzylidene cyclopentanone dye for one- and two-photon photopolymerization, Eur. Polym. J. 162 (2022) 110917. https://doi.org/10.1016/j.eurpolymj.2021.110917.

[355] L. Poocza, M. Gottschaldt, E. Markweg, N. Hauptmann, G. Hildebrand, D. Pretzel, M. Hartlieb, C. Reichardt, J. Kübel, U.S. Schubert, O. Mollenhauer, B. Dietzek, K. Liefeith, Optimized Photoinitiator for Fast Two-Photon Absorption Polymerization of Polyester-Macromers for Tissue Engineering, Adv. Eng. Mater. 19 (2017) 1600686. https://doi.org/10.1002/adem.201600686.

[356] J. Wu, Y. Zhao, X. Li, M. Shi, F. Wu, X. Fang, Multibranched benzylidene cyclopentanone dyes with large two-photon absorption cross-sections, New J. Chem. 30 (2006) 1098–1103. https://doi.org/10.1039/B604695A.

[357] A. Al Rashid, W. Ahmed, M.Y. Khalid, M. Koç, Vat photopolymerization of polymers and polymer composites: Processes and applications, Addit. Manuf. 47 (2021) 102279. https://doi.org/10.1016/j.addma.2021.102279.

[358] M.M. Hausladen, B. Zhao, M.S. Kubala, L.F. Francis, T.M. Kowalewski, C.J. Ellison, Synthetic growth by self-lubricated photopolymerization and extrusion inspired by

plants and fungi, Proc. Natl. Acad. Sci. 119 (2022) e2201776119. https://doi.org/10.1073/pnas.2201776119.

[359] R. Nazir, F. Bourquard, E. Balčiūnas, S. Smoleń, D. Gray, N.V. Tkachenko, M. Farsari, D.T. Gryko, π-Expanded α,β-Unsaturated Ketones: Synthesis, Optical Properties, and Two-Photon-Induced Polymerization, ChemPhysChem. 16 (2015) 682–690. https://doi.org/10.1002/cphc.201402646.

[360] H. Meier, Conjugated Oligomers with Terminal Donor–Acceptor Substitution, Angew. Chem. Int. Ed. 44 (2005) 2482–2506. https://doi.org/10.1002/anie.200461146.

[361] G. Lemercier, C. Martineau, J.-C. Mulatier, I. Wang, O. Stéphan, P. Baldeck, C. Andraud, Analogs of Michler's ketone for two- photon absorption initiation of polymerization in the near infrared: synthesis and photophysical properties, New J. Chem. 30 (2006) 1606–1613. https://doi.org/10.1039/B608391A.

[362] K.M. Shafeekh, S. Das, C. Sissa, A. Painelli, Asymmetric Squaraine Dyes: Spectroscopic and Theoretical Investigation, J. Phys. Chem. B. 117 (2013) 8536–8546. https://doi.org/10.1021/jp401099g.

[363] F. Momicchioli, G. Ponterini, D. Vanossi, Linear and nonlinear optical properties of V-shaped D–π–A–π–D chromophores: effects of the incorporation of aromatic rings in the polyenic π-bridges of open-chain ketocyanines, Phys. Chem. Chem. Phys. 16 (2014) 15576–15589. https://doi.org/10.1039/C4CP01564A.

[364] R. Nazir, P. Danilevicius, A.I. Ciuciu, M. Chatzinikolaidou, D. Gray, L. Flamigni, M. Farsari, D.T. Gryko, π-Expanded Ketocoumarins as Efficient, Biocompatible Initiators for Two-Photon-Induced Polymerization, Chem. Mater. 26 (2014) 3175–3184. https://doi.org/10.1021/cm500612w.

[365] G. Jones, P.T. Xuan, W. Schwarz, Singlet sensitization of the norbornadiene rearrangement: excitation energy cascade potentially involving triplet exciplexes, Tetrahedron Lett. 23 (1982) 5505–5508. https://doi.org/10.1016/S0040-4039(00)85879-7.

[366] A.K. Sen, B. Mukherjee, A.S. Bhattacharyya, P.P. De, A.K. Bhowmick, Kinetics of silane grafting and moisture crosslinking of polyethylene and ethylene propylene rubber, J. Appl. Polym. Sci. 44 (1992) 1153–1164. https://doi.org/10.1002/app.1992.070440704.

[367] D.P. Specht, P.A. Martic, S. Farid, Ketocoumarins: A new class of triplet sensitizers, Tetrahedron. 38 (1982) 1203–1211. https://doi.org/10.1016/0040-4020(82)85104-1.

[368] X. Li, Y. Zhao, T. Wang, M. Shi, F. Wu, Coumarin derivatives with enhanced two-photon absorption cross-sections, Dyes Pigments. 74 (2007) 108–112. https://doi.org/10.1016/j.dyepig.2006.01.020.

[369] A.S. Melnikov, P.Y. Serdobintsev, A.D. Vedyaykin, M.A. Khodorkovskii, Two-photon absorption cross section for Coumarins 102, 153 and 307, J. Phys. Conf. Ser. 917 (2017) 062029. https://doi.org/10.1088/1742-6596/917/6/062029.

[370] S. Inacker, J. Fanelli, S.I. Ivlev, N.A. Hampp, Intramolecular Coumarin-Dimer Containing Polyurethanes: Optical Tuning via Single- and Two-Photon Absorption Processes, Macromolecules. (2022). https://doi.org/10.1021/acs.macromol.2c01374.

[371] M. Klausen, V. Dubois, G. Clermont, C. Tonnelé, F. Castet, M. Blanchard-Desce, Dual-wavelength efficient two-photon photorelease of glycine by π-extended dipolar coumarins, Chem. Sci. 10 (2019) 4209–4219. https://doi.org/10.1039/C9SC00148D.

[372] P. Garra, B. Graff, F. Morlet-Savary, C. Dietlin, J.-M. Becht, J.-P. Fouassier, J. Lalevée, Charge Transfer Complexes as Pan-Scaled Photoinitiating Systems: From 50 μm 3D Printed Polymers at 405 nm to Extremely Deep Photopolymerization (31 cm), Macromolecules. 51 (2018) 57–70. https://doi.org/10.1021/acs.macromol.7b02185.

[373] P. Imrie, J. Jin, Polymer 4D printing: Advanced shape-change and beyond, J. Polym. Sci. 60 (2022) 149–174. https://doi.org/10.1002/pol.20210718.

[374] H.Y. Jeong, B.H. Woo, N. Kim, Y.C. Jun, Multicolor 4D printing of shape-memory polymers for light-induced selective heating and remote actuation, Sci. Rep. 10 (2020) 6258. https://doi.org/10.1038/s41598-020-63020-9.

[375] Z. Zhang, N. Corrigan, A. Bagheri, J. Jin, C. Boyer, A Versatile 3D and 4D Printing System through Photocontrolled RAFT Polymerization, Angew. Chem. 131 (2019) 18122–18131. https://doi.org/10.1002/ange.201912608.

[376] Y. Zhang, L. Josien, J.-P. Salomon, A. Simon-Masseron, J. Lalevée, Photopolymerization of Zeolite/Polymer-Based Composites: toward 3D and 4D Printing Applications, ACS Appl. Polym. Mater. 3 (2021) 400–409. https://doi.org/10.1021/acsapm.0c01170.

[377] X. Wan, Y. Zhao, J. Xue, F. Wu, X. Fang, Water-soluble benzylidene cyclopentanone dye for two-photon photopolymerization, J. Photochem. Photobiol. Chem. 202 (2009) 74–79. https://doi.org/10.1016/j.jphotochem.2008.10.029.

[378] H.Y. Woo, J.W. Hong, B. Liu, A. Mikhailovsky, D. Korystov, G.C. Bazan, Water-Soluble [2.2]Paracyclophane Chromophores with Large Two-Photon Action Cross Sections, J. Am. Chem. Soc. 127 (2005) 820–821. https://doi.org/10.1021/ja0440811.

[379] H.Y. Woo, B. Liu, B. Kohler, D. Korystov, A. Mikhailovsky, G.C. Bazan, Solvent Effects on the Two-Photon Absorption of Distyrylbenzene Chromophores, J. Am. Chem. Soc. 127 (2005) 14721–14729. https://doi.org/10.1021/ja052906g.

[380] A. Nag, D. Goswami, Solvent effect on two-photon absorption and fluorescence of rhodamine dyes, J. Photochem. Photobiol. Chem. 206 (2009) 188–197. https://doi.org/10.1016/j.jphotochem.2009.06.007.

[381] Z. Li, J. Torgersen, A. Ajami, S. Mühleder, X. Qin, W. Husinsky, W. Holnthoner, A. Ovsianikov, J. Stampfl, R. Liska, Initiation efficiency and cytotoxicity of novel water-soluble two-photon photoinitiators for direct 3D microfabrication of hydrogels, RSC Adv. 3 (2013) 15939–15946. https://doi.org/10.1039/C3RA42918K.

[382] A. Ovsianikov, S. Mühleder, J. Torgersen, Z. Li, X.-H. Qin, S. Van Vlierberghe, P. Dubruel, W. Holnthoner, H. Redl, R. Liska, J. Stampfl, Laser Photofabrication of Cell-Containing Hydrogel Constructs, Langmuir. 30 (2014) 3787–3794. https://doi.org/10.1021/la402346z.

[383] W. Yang, Q. Zou, Y. Zhou, Y. Zhao, N. Huang, Y. Gu, F. Wu, Carboxylate modified benzylidene cyclopentanone dyes for one- and two-photon excited photodynamic therapy, J. Photochem. Photobiol. Chem. 222 (2011) 228–235. https://doi.org/10.1016/j.jphotochem.2011.06.002.

[384] J. Li, X. Zhang, J. Nie, X. Zhu, Visible light and water-soluble photoinitiating system based on the charge transfer complex for free radical photopolymerization, J. Photochem. Photobiol. Chem. 402 (2020) 112803. https://doi.org/10.1016/j.jphotochem.2020.112803.

[385] S.-J. Chung, K.-S. Kim, T.-C. Lin, G.S. He, J. Swiatkiewicz, P.N. Prasad, Cooperative Enhancement of Two-Photon Absorption in Multi-branched Structures, J. Phys. Chem. B. 103 (1999) 10741–10745. https://doi.org/10.1021/jp992846z.

[386] P. Macak, Y. Luo, P. Norman, H. Ågren, Electronic and vibronic contributions to two-photon absorption of molecules with multi-branched structures, J. Chem. Phys. 113 (2000) 7055–7061. https://doi.org/10.1063/1.1313559.

[387] I. Polyzos, G. Tsigaridas, M. Fakis, V. Giannetas, P. Persephonis, J. Mikroyannidis, Two-photon absorption properties of novel organic materials for three-dimensional optical

memories, Chem. Phys. Lett. 369 (2003) 264–268. https://doi.org/10.1016/S0009-2614(02)01969-3.

[388] L. Porrès, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz, M. Blanchard-Desce, Enhanced Two-Photon Absorption with Novel Octupolar Propeller-Shaped Fluorophores Derived from Triphenylamine, Org. Lett. 6 (2004) 47–50. https://doi.org/10.1021/ol036041s.

[389] H. Wang, Z. Li, P. Shao, Y. Liang, H. Wang, J. Qin, Q. Gong, Synthesis and properties of new two-photon absorption chromophores containing 3,5-dicyano-2,4,6-tristyrylpyridine as the core, New J. Chem. 29 (2005) 792–797. https://doi.org/10.1039/B416860G.

[390] J. Wu, M. Shi, Y. Zhao, F. Wu, Two-photon absorption property and photopolymerization sensitizing efficiency of asymmetrical benzylidene cyclopentanone dyes, Dyes Pigments. 76 (2008) 690–695. https://doi.org/10.1016/j.dyepig.2007.01.007.

[391] H. Gruen, H. Goerner, Trans .fwdarw. cis photoisomerization, fluorescence, and relaxation phenomena of trans-4-nitro-4′-(dialkylamino)stilbenes and analogues with a nonrotatable amino group, J. Phys. Chem. 93 (1989) 7144–7152. https://doi.org/10.1021/j100357a024.

[392] D. Beljonne, J.L. Brédas, M. Cha, W.E. Torruellas, G.I. Stegeman, J.W. Hofstraat, W.H.G. Horsthuis, G.R. Möhlmann, Two-photon absorption and third-harmonic generation of di-alkyl-amino-nitro-stilbene (DANS): A joint experimental and theoretical study, J. Chem. Phys. 103 (1995) 7834–7843. https://doi.org/10.1063/1.470200.

[393] J. Xue, Y. Zhao, J. Wu, F. Wu, Novel benzylidene cyclopentanone dyes for two-photon photopolymerization, J. Photochem. Photobiol. Chem. 195 (2008) 261–266. https://doi.org/10.1016/j.jphotochem.2007.10.012.

[394] E. Lippert, Dipolmoment und Elektronenstruktur von angeregten Molekülen, Z. Für Naturforschung A. 10 (1955) 541–545. https://doi.org/10.1515/zna-1955-0707.

[395] N. Mataga, Y. Kaifu, M. Koizumi, The Solvent Effect on Fluorescence Spectrum, Change of Solute-Solvent Interaction during the Lifetime of Excited Solute Molecule, Bull. Chem. Soc. Jpn. 28 (1955) 690–691. https://doi.org/10.1246/bcsj.28.690.

[396] X. Wang, Y. Fang, Q. Zou, Y. Zhao, F. Wu, Initiation efficiency and cytotoxicity of a series of water-soluble benzylidene cyclopentanone for two-photon polymerization, in: Opt. Health Care Biomed. Opt. VI, SPIE, 2014: pp. 264–269. https://doi.org/10.1117/12.2071644.

[397] M. Rahal, H. Bidotti, S. Duval, B. Graff, T. Hamieh, J. Toufaily, F. Dumur, J. Lalevée, Investigation of pyrene vs Anthracene-based oxime esters: Role of the excited states on their polymerization initiating abilities, Eur. Polym. J. 177 (2022) 111452. https://doi.org/10.1016/j.eurpolymj.2022.111452.

[398] J. Akhigbe, M. Luciano, M. Zeller, C. Brückner, Mono- and Bisquinoline-Annulated Porphyrins from Porphyrin β,β′-Dione Oximes, J. Org. Chem. 80 (2015) 499–511. https://doi.org/10.1021/jo502511j.

[399] AllonasXavier, LalevéeJacques, FouassierJean-Pierre, TachiHideki, ShiraiMasamitsu, TsunookaMasahiro, Triplet State of O-Acyloximes Studied by Time-Resolved Absorption Spectroscopy, Chem. Lett. (2004). https://doi.org/10.1246/cl.2000.1090.

[400] G.A. Delzenne, U. Laridon, H. Peeters, Photopolymerization initiated by O-acyloximes, Eur. Polym. J. 6 (1970) 933–943. https://doi.org/10.1016/0014-3057(70)90028-5.

[401] D.E. Fast, A. Lauer, J.P. Menzel, A.-M. Kelterer, G. Gescheidt, C. Barner-Kowollik, Wavelength-Dependent Photochemistry of Oxime Ester Photoinitiators, Macromolecules. 50 (2017) 1815–1823. https://doi.org/10.1021/acs.macromol.7b00089.

[402] F.A. Via, Sensitization of glyoxylate photoinitiators, EP0127765A1, 1984. https://patents.google.com/patent/EP0127765A1/en (accessed March 4, 2022).

[403] X. He, Y. Gao, J. Nie, F. Sun, Methyl Benzoylformate Derivative Norrish Type I Photoinitiators for Deep-Layer Photocuring under Near-UV or Visible LED, Macromolecules. 54 (2021) 3854–3864. https://doi.org/10.1021/acs.macromol.0c02868.

[404] M. Bouzrati-Zerelli, J. Kirschner, C.P. Fik, M. Maier, C. Dietlin, F. Morlet-Savary, J.P. Fouassier, J.-M. Becht, J.E. Klee, J. Lalevée, Silyl Glyoxylates as a New Class of High Performance Photoinitiators: Blue LED Induced Polymerization of Methacrylates in Thin and Thick Films, Macromolecules. 50 (2017) 6911–6923. https://doi.org/10.1021/acs.macromol.7b01370.

[405] P. Garra, J.P. Fouassier, S. Lakhdar, Y. Yagci, J. Lalevée, Visible light photoinitiating systems by charge transfer complexes: Photochemistry without dyes, Prog. Polym. Sci. 107 (2020) 101277. https://doi.org/10.1016/j.progpolymsci.2020.101277.